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# THERMODYNAMICS





# THERMODYNAMICS

By EDWARD F. OBERT

*Associate Professor of Mechanical Engineering  
Northwestern Technological Institute  
Northwestern University*

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## **THERMODYNAMICS**

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To  
H.F.O.



## PREFACE

This book has been written to serve as a fundamental text in the fields of thermodynamics and heat power. The presentation is believed to be sufficiently rigorous and complete to satisfy the student and to serve as an introduction to more advanced topics that may be given in later courses.

Although ample material is included for a course that extends through three semesters, each containing four recitation periods a week, it is most probable that the book will be used for a two-semester course in thermodynamics. Because of this probability, many of the chapters have been developed as separate entities to allow the teacher freedom of presentation and rearrangement. The custom of supplying only the exact material that the student must master in order to satisfy the minimum requirements of the course is deplored by the author. In this text each chapter is more than sufficient for the undergraduate requirements and the arrangement of material encourages the student to progress beyond the borders prescribed by the teacher. The author believes this method of presentation is superior to the older method, which relegates advanced topics to separate chapters that become unused appendixes to the book.

The text material should be entirely sufficient for the undergraduate curriculum without the necessity for further specialized courses on particular phases of engineering. To those who disagree with this viewpoint it is suggested that the text be supplemented by the engineering guides and technical preprints to form not only a complete textbook for the beginner, but also the pattern of study followed by the successful engineer.

The author also suggests that no justification exists for separate courses in thermodynamics and heat power. These subjects should be combined into one course with at least two textbooks. Then, as the student is introduced to the First Law, for example, the illustrative material that is found in the heat-power textbook can be used to full advantage to supplement the thermodynamic principles. A single textbook for such a course is impractical because the size would be

excessive, and undesirable because a line of demarcation does exist and should be clearly evident to the student

The reasons for writing the book are many. The first objective is to present and emphasize certain essential material that must be thoroughly understood by the practicing engineer, since most students will not in later life be research workers or teachers. To accomplish this purpose the text stresses real machines, flow processes, properties of fluids, and the conditions where simplified analyses can be applied. Nothing in this procedure will adversely affect a future graduate student

The second objective of the text is to emphasize the continuity of thought leading to the Second Law. To accomplish this purpose, the First Law, its applications, and its limitations are stressed before the Second Law is introduced, while study of the characteristics of fluids is delayed until after the significance of the concepts of temperature and entropy is presented. It is not intended that the first five chapters be exhaustively covered in the classroom even though complete mastery of these subjects is a necessary part of thermodynamics.

The third objective of the text is to show that for many real fluids and for many real processes the simple perfect-gas laws are an adequate and most desirable means of analysis, at least for engineers who use slide rules for computations. To accomplish this purpose the properties of real fluids are presented and approximate solutions are studied before the concept of a perfect gas is introduced, moreover, comparison between real and perfect gases is stressed.

The kinetic theory is used as a logical means for introducing the student to the characteristics of real gases. Although thermodynamics does not need the kinetic theory for this introduction, still there is no reason for denying to the student this help in understanding a complex subject.

The flow of fluids has been emphasized because the problem of fluid flow is one of the most usual tasks that the practicing engineer is called upon to treat, for the same reason, irreversible processes are stressed. Necessarily, then, the subject matter becomes somewhat difficult to master, yet the student must learn more than the ability to use a slide rule if he is to understand thermodynamics.

The introductory chapter on dimensions and units is included because junior engineering students do not understand this subject. The importance of this "hidden half of the problem" is emphasized by making it the first chapter of the text. It is regrettable that a chapter of this type must be included in a junior engineering text, but the

author feels that this fundamental material must be available to the student at the start of the usual sequence of thermodynamics and heat transfer. It is not intended that this chapter be exhaustively covered.

Many persons have directly or indirectly contributed to this book. The aid and encouragement of Herbert S. Philbrick, Emeritus Professor of Thermodynamics, Northwestern University, was particularly appreciated. The author wishes to thank and acknowledge indebtedness to his colleagues who gave so generously of their time and advice: Irwin T. Wetzel, William H. Roberts, and Donald R. Diggs used the mimeographed text in their classes and helped in the revision made necessary by teaching experiences, Irwin T. Wetzel and George M. Brown critically reviewed much of the final manuscript, Harrison Hayford, of the Northwestern University English department, was the editorial advisor, Willard L. Rogers, Joel F. Bailey, Virgil C. Williams, and Dean Ovid W. Eshbach gave advice on specialized subjects. The illustrations were drawn by Raymond Dost. The typing of the manuscript was in the able hands of Katherine Kropf and Marcy Puster, although the author's sister, Ethel, and his wife, Helen, contributed greatly and also typed the first copy from the handwritten draft.

EDWARD F. OBERT

EVANSTON, ILL.

*June, 1948*





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## CHAPTER I

### SURVEY OF DIMENSIONS AND UNITS

Before attempting a study of engineering, the dimensions and units to be encountered must be thoroughly understood. Dimensions are descriptions that allow more complicated situations to be described in terms of simpler, more basic definitions.

**1-1. Dimensions.** A *dimension* can be defined as a name describing certain qualities or characteristics of an entity. In this sense all names are dimensions, and an infinite number of dimensions is possible. To reduce this number, certain descriptions may be expressed in terms of other more basic descriptions (dimensions). For example, length, area, and volume are dimensions describing certain characteristics of an object. But since an area can be conceived and measured as a length squared, and a volume as a length cubed, in place of these dimensions all these descriptions can be stated in terms of some fundamental dimension, in this case, length. In equational form,

$$[A] = [L^2] \quad (a)$$

$$[V] = [L^3] \quad (b)$$

The bracket is used to identify a dimension, and the above equations should be read

Eq (a) The dimension of area is equivalent to the dimension of length squared

Eq (b) The dimension of volume is equivalent to the dimension of length cubed

By following this procedure, a large number of dimensions can be reduced to a much smaller number of *fundamental*, *basic*, or *primary* dimensions. All other dimensions expressed in terms of these fundamental descriptions are known as *secondary* or *derived* dimensions. In the foregoing example, area and volume have derived dimensions in terms of the fundamental dimension of length.

**1-2. Engineering Units for the Fundamental Dimensions.** While a dimension is a descriptive word picture, a *unit* is a definite standard

or measure of a dimension. A *unit* can be defined as a particular amount of the quantity to be measured. For example, foot, yard, inch, rod, and meter are all different units specifying different but definite lengths, while the common dimension of all these units is length.

The units commonly used in engineering are defined as follows

*Time.* The *second* (sec) is the fundamental unit of time and is defined as  $1/86,400$  part of a mean solar day.

*Length.* The *foot* (ft) is the fundamental unit of length and is defined as  $\frac{1}{3}$  *yard* (yd) where the *yard* is  $3,600/3,937$  the length of the *meter* (m). The *meter* is the distance between two lines, measured at 0 degrees centigrade, on a platinum-iridium bar that is kept at the International Bureau of Weights and Measures at Sèvres, France. A meter is equivalent to 100 *centimeters* (cm).

*Mass.* The *pound* (avoirdupois) ( $\text{lb}_m$ ) is the fundamental unit of mass and is defined as 453 5924277 *grams* (g). The *kilogram* (kg) by international agreement is a certain basic mass of platinum-iridium located in Sèvres, France. The *slug* is defined as the mass that can be accelerated  $1 \text{ ft sec}^{-2}$  when acted upon by a standard force pound ( $\text{lb}_f$ ). 1 *slug* is equivalent to 32 1739 pounds mass ( $\text{lb}_m$ ).

*Force.* The *standard force pound* ( $\text{lb}_f$ ) is the fundamental unit of force and is defined as the force necessary to accelerate the mass pound ( $\text{lb}_m$ ) at a rate of  $32 \text{ 1739 ft sec}^{-2}$ . The *poundal* is defined as the force required to accelerate the mass pound ( $\text{lb}_m$ ) at a rate of  $1 \text{ ft sec}^{-2}$ . It is not in common use.

*Acceleration of Gravity.* The *standard acceleration of gravity* (by international agreement) is  $g_0 = 32 \text{ 1739 ft sec}^{-2} = 980 \text{ 665 cm sec}^{-2}$ . The *local* acceleration of gravity will be designated by the symbol  $g$ .

Upon examination a serious fault appears in the above list of units. The name *pound* is assigned to the fundamental units of both mass and force; yet obviously a *pound of mass* is an entirely different type of thing from a *pound of force*. To overcome this difficulty the terms *force pound* (or *pound force*) and *mass pound* (or *pound mass*) will be used and abbreviated  $\text{lb}_f$  and  $\text{lb}_m$  for identification.

### 1-3. Dimensional Systems with Three Fundamental Dimensions.

A dimensional system that will completely describe the events that occur in the science of mechanics can be constructed from the fundamental dimensions. It would appear that the dimensions of time [ $\theta$ ], length [ $L$ ], mass [ $M$ ], and force [ $F$ ] would be the minimum number of basic dimensions necessary to form a complete dimensional system. But for one of these four descriptions it is possible to find derived

dimensions by using Newton's law, namely,

$$\text{Force} \sim \text{mass} \times \text{acceleration}$$

This proportionality can be written in equational form as

$$F = Cma$$

where  $C$  is a constant. If it is desired to express the equation without the constant, for dimensional equality

$$[F] = [M][a] \quad (a)$$

Now acceleration need not be a primary dimension because it can be measured in terms of length  $[L]$  and time  $[\theta]$

$$\text{Velocity } [V] = \frac{[L]}{[\theta]}$$

and

$$\text{Acceleration } [a] = \frac{[V]}{[\theta]} = \frac{[L]}{[\theta^2]} = [L\theta^{-2}]$$

Substitution in Eq (a) gives

$$[F] = [M][L\theta^{-2}] = [ML\theta^{-2}]$$

Thus, the fundamental dimension, force  $[F]$ , can be given the derived dimension of  $ML\theta^{-2}$ , and thereby a system of dimensions can be constructed involving only mass  $[M]$ , length  $[L]$ , and time  $[\theta]$ . This is called the  $ML\theta$  system of dimensions.

In the  $ML\theta$  system, the English units are the pound mass  $[M]$ , the foot  $[L]$ , and the second  $[\theta]$ . With these units substituted in the Newtonian equation

$$F = ma$$

$$\begin{aligned} (1 \text{ unit force } [ML\theta^{-2}]) &= (1 \text{ pound mass } [M]) \left( \frac{1 \text{ ft } [L]}{1 \text{ sec}^2 [\theta^2]} \right) \quad (b) \\ [ML\theta^{-2}] &= [ML\theta^{-2}] \end{aligned}$$

This equation is *dimensionally homogeneous* because each term of the equation has the dimension  $ML\theta^{-2}$ . Here the unit of force has derived dimensions, and it is called the *poundal*. The size of the poundal must satisfy Eq (b). *The poundal is the force required to accelerate 1 pound mass at the rate of 1 ft sec<sup>-2</sup>*. It must be remembered in using this system that

$$1 \text{ poundal} = \frac{1 \text{ lb}_m \text{ ft}}{\text{sec}^2}$$

However, the poundal is rarely used.



An alternative system can be constructed by allowing the Newtonian equation to define the dimensions of mass.

$$F = ma$$

$$[M] = \frac{[F]}{[a]} = \frac{[F]}{[L\theta^{-2}]} = [FL^{-1}\theta^2]$$

Here the fundamental dimension of mass is given the derived dimension of  $FL^{-1}\theta^2$ , and a system is constructed that involves only force  $[F]$ , length  $[L]$ , and time  $[\theta]$ . This is called the  $FL\theta$  system.

In the  $FL\theta$  system the English units are the pound force  $[F]$ , the foot  $[L]$ , and the second  $[\theta]$ . These units can be substituted in the equation

$$F = ma$$

$$(1 \text{ pound force } [F]) = (1 \text{ unit mass } [FL^{-1}\theta^2]) \left( \frac{1 \text{ ft } [L]}{1 \text{ sec}^2 [\theta^2]} \right) \quad (c)$$

$$[F] = [F]$$

Here the unit of mass has derived dimensions of  $FL^{-1}\theta^2$ , and it is called the *slug*. The size of the *slug* is determined by Eq. (c). *The slug is the mass that can be accelerated 1 ft sec<sup>-2</sup> by a force of 1 standard pound force.* In using this system it must be remembered that

$$1 \text{ slug} = 1 \frac{\text{lb}_f \text{ sec}^2}{\text{ft}}$$

**1-4. Nonunitary Homogeneous Equations and the Conversion of Units.** Equations are often used to show the relative size of different units.

$$5,280 \text{ feet} = 1 \text{ mile}$$

$$[L] = [L]$$

$$3,600 \text{ seconds} = 1 \text{ hour}$$

$$[\theta] = [\theta]$$

Inspection of these equations shows that they are dimensionally correct because all terms have the same dimensions. However, the equations do not have *unitary homogeneity* because the terms are expressed in different units. Because of this nonhomogeneity, there are some who prefer to show the equality in the form of a dimensionless ratio that has a value of unity

$$5,280 \frac{\text{ft}}{\text{mile}} = 1$$

$$3,600 \frac{\text{sec}}{\text{hr}} = 1$$

These unit conversion factors can be used as multiplying factors because it is always permissible to multiply (or divide) by unity.

**Example 1:** Convert  $88 \frac{\text{ft}}{\text{sec}}$  to miles per hour (mph).

**Solution:** From Table I (Appendix) or from memory select the appropriate unit conversion factors, namely,

$$5,280 \frac{\text{ft}}{\text{mile}} \quad 3,600 \frac{\text{sec}}{\text{hr}}$$

Now arrange these factors of unity to cancel the units of feet and seconds

$$88 \frac{\text{ft}}{\text{sec}} \frac{\text{mile}}{5,280 \text{ ft}} \frac{3,600 \text{ sec}}{\text{hr}} = \frac{88(3,600)}{5,280} \frac{\text{mile}}{\text{hr}} = 60 \text{ mph} \quad \text{Ans}$$

**Example 2:** Repeat Example 1 but use the defining equations

**Solution:** Substituting

$$\begin{aligned} 5,280 \text{ ft} &= 1 \text{ mile} \\ 3,600 \text{ sec} &= 1 \text{ hr} \end{aligned}$$

in  $88 \frac{\text{ft}}{\text{sec}}$  results in

$$88 \frac{\text{ft}}{\text{sec}} = 88 \frac{1 \text{ ft}}{1 \text{ sec}} = 88 \frac{\frac{1}{5,280} \text{ mile}}{\frac{1}{3,600} \text{ hr}} = 88 \frac{3,600 \text{ mile}}{5,280 \text{ hr}} = 60 \text{ mph} \quad \text{Ans}$$

Both the poundal and the slug can be expressed as unit conversion factors, consider first the slug. By definition, 1 standard pound force will accelerate 1 slug mass at the rate of  $1 \text{ ft sec}^{-2}$ , it will also accelerate 1 pound mass at the rate of  $32 \text{ } 1739 \text{ ft sec}^{-2}$  (Art 1-2). It follows that the slug is a definite quantity of matter of size 32 1739 times that of the pound mass. Therefore, it is permissible to write

$$1 \text{ slug} = 32 \text{ } 1739 \text{ lb}_m$$

where the dimensions are conceived to be

$$[M] = [M]$$

and also

$$32 \text{ } 1739 \frac{\text{lb}_m}{\text{slug}} = 1 \quad (\text{a})$$

In similar manner recall that, by definition (Art 1-2), 1 standard force pound will accelerate 1 pound mass at the rate of  $32 \text{ } 1739 \text{ ft sec}^{-2}$ , a poundal will accelerate 1 pound mass at the rate of  $1 \text{ ft sec}^{-2}$ . Consequently, the poundal is a definite force of size  $1/32 \text{ } 1739$  that of the standard pound force. Therefore, it is permissible to write

$$32 \text{ } 1739 \text{ poundals} = 1 \text{ lb}_f$$

where the dimensions are thought of as

$$[F] = [F]$$

and

$$32\,1739 \frac{\text{poundals}}{\text{lb}_f} = 1 \quad (b)$$

Equations (a) and (b), like the factors of feet and mile, second and hour, are *unit conversion factors*

**1-5. The Engineering Dimensional System.** Although it is recognized that a dimensional system can be constructed from only three fundamental dimensions, nevertheless, in engineering a system involving four fundamental dimensions is in common use. It is called the *FMLθ system* of dimensions. In this system the unit of force is the pound force  $[F]$ ; the unit of mass is the pound mass  $[M]$ , the unit of length is the foot  $[L]$ , and the unit of time is the second  $[\theta]$ . The procedure in constructing the dimensional system can be illustrated as before by the Newtonian equation

$$F \sim \text{mass} \times \text{acceleration}$$

This proportionality can be written as an equation:

$$\frac{F}{F'} = \frac{ma}{m'a'} \quad (a)$$

and

$$F = \frac{1}{\frac{m'a'}{F'}} ma \quad (b)$$

Equations (a) and (b) are dimensionally homogeneous for any system of units

Recall that, by definition, 1  $\text{lb}_f$  will accelerate 1  $\text{lb}_m$  at the rate of 32.1739  $\text{ft sec}^{-2}$ , and substitute these values in Eq (a).

$$\frac{F}{1 \text{ lb}_f} = \frac{ma}{32\,1739 \text{ lb}_m \frac{\text{ft}}{\text{sec}^2}}$$

Upon rearranging, as in Eq (b),

$$F = \frac{1}{32\,1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}} ma$$

which is usually written

$$F = \frac{1}{g_c} ma \quad (c)$$

Here  $g_c$  is called a *dimensional constant*.

$$g_c = 32\,1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}$$

$$[g_c] = \left[ \frac{ML}{F\theta^2} \right]$$

Note that  $g_c$  is not the acceleration of gravity because it has different dimensions (although the number 32 1739 is equal to that of the standard acceleration of gravity)

**Example 3:** Determine the force necessary to accelerate 10 lb<sub>m</sub> at the rate of 10 ft sec<sup>-2</sup>

**Solution:** In the engineering system, the dimensions of force, mass, and acceleration are related by the equation

$$F = \frac{1}{g_c} ma$$

and

$$\begin{aligned} F &= \frac{1}{g_c} 10 \text{ lb}_m 10 \text{ ft sec}^{-2} \\ &= \frac{100 \text{ lb}_m \text{ ft sec}^{-2}}{32\,1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}} \\ &= 3\,105 \text{ lb}_f \quad \text{Ans.} \end{aligned}$$

**Example 4** Determine the force exerted by 10 lb<sub>m</sub> because of the attraction of gravity at a location where  $g = g_0$

**Solution**

$$\begin{aligned} F &= \frac{1}{g_c} ma \\ &= \frac{1}{g_c} 10 \text{ lb}_m g_0 \\ &= \frac{321\,739 \text{ ft sec}^{-2} \text{ lb}_m}{32\,1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}} \\ &= 10 \text{ lb}_f \quad \text{Ans} \end{aligned}$$

Inspection of Eq (c)

$$F = \frac{1}{g_c} ma$$

shows that the dimensional constant  $g_c$  can be used as a dimensional conversion factor.

The dimension of mass can be eliminated from a quantity by dividing by  $g_c$ ; the dimension of force can be eliminated from a quantity by multiplying by  $g_c$ .

**Example 5:** Eliminate the dimension of force from  $5\,00(10^{-9})\text{ lb}_f\text{ ft}^{-1}\text{ hr}$ .

**Solution:** The easiest solution is to multiply by  $g_c$  and  $3,600\frac{\text{sec}}{\text{hr}}$

$$\left(5\,00(10^{-9})\frac{\text{lb}_f\text{ hr}}{\text{ft}^2}\right)\left(\frac{3,600\text{ sec}}{\text{hr}}\right)\left(\frac{32\,1739\text{ lb}_m\text{ ft}}{\text{lb}_f\text{ sec}^2}\right)$$

$$(5\,00)(3,600)(32\,1739)(10^{-9})\frac{\text{lb}_m}{\text{ft sec}} = 57\,9(10^{-5})\frac{\text{lb}_m}{\text{ft sec}} \quad \text{Ans}$$

(Of course, the answer could have been found in units of  $\text{lb}_m/\text{ft hr}$ )

It has been demonstrated that a four-fundamental-dimension system can be constructed for the engineering units of pound mass, pound force, foot, and second. The same reasoning can be used to devise a system of four fundamental dimensions employing as units the slug, pound force, foot, and second (or a system employing the poundal, pound mass, foot, and second). It will be found that the dimensional constants for the English systems of units are

$$g_c = 32\,1739\frac{\text{lb}_m\text{ ft}}{\text{lb}_f\text{ sec}^2} = 1\frac{\text{slug ft}}{\text{lb}_f\text{ sec}^2} = 1\frac{\text{lb}_m\text{ ft}}{\text{poundal sec}^2}$$

TABLE 1-1 — DIMENSIONAL SYSTEMS AND UNITS

Quantity	Name of systems			
	Absolute English, $ML\theta$	Absolute metric, $ML\theta$	Technical English, $FL\theta$	Engineering English, $FML\theta$
Length	foot	centimeter	foot	foot
Time	second	second	second	second
Mass	pound mass	gram	slug	pound mass
Force	poundal	dyne	pound force	pound force
Power	foot poundal/sec	erg/sec	foot lb <sub>f</sub> /sec	foot lb <sub>f</sub> /sec
Energy	foot poundal	erg	foot lb <sub>f</sub>	foot lb <sub>f</sub>
Dimensional constant $g_c$	$1\text{ lb}_m\text{ ft}$ $\text{poundal sec}^2$	$1\text{ g cm}$ $\text{dyne sec}^2$	$1\text{ slug ft}$ $\text{lb}_f\text{ sec}^2$	$32\,1739\text{ lb}_m\text{ ft}$ $\text{lb}_f\text{ sec}^2$

**1-6. The Dimensional Constant as a Unit Conversion Factor.** Although the dimensional constant  $g_c$  acknowledges the existence of four fundamental dimensions, still, Newton's law shows that only three basic dimensions are necessary for a complete dimensional

**system** Because of this fact the dimensional constant can always be treated as a unit conversion factor. In other words, the units for the dimensional system bear a definite relationship to each other, and this relationship is established by Newton's law whether or not a fourth basic dimension is premised. For example, there are 32 1739 lb<sub>m</sub> (units) in 1 slug (unit) of mass, this is shown by the unit conversion factor

$$32\,1739 \frac{\text{lb}_m}{\text{slug}} = 1 \quad (a)$$

The equivalent units for the slug, by Newton's law, are

$$1 \text{ slug} = 1 \frac{\text{lb}_f \text{ sec}^2}{\text{ft}}$$

When this factor is substituted in Eq. (a) the result is

$$32\,1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2} = 1$$

and this is recognized to be the dimensional constant  $g_c$ . Thus, the philosophy of this article shows that  $g_c$  can be considered to be a unit conversion factor with absolute value of unity. For this reason  $g_c$  can be used at will as a multiplying or dividing factor irrespective of the origin of the quantities that are to be operated upon. In Example 5,  $g_c$  was considered to be a dimensional constant that was used to eliminate an undesired *dimension*, it could also be considered that  $g_c$  was merely a unit conversion factor that eliminated an undesired *unit*. Whether  $g_c$  is regarded as a dimensional or unit conversion factor is relatively unimportant, for the same result will be obtained from either viewpoint. In this text  $g_c$  is used, most often, as a dimensional constant.

**1-7 Other Dimensional Systems and Units.<sup>1</sup>** The English system of units in the ML $\theta$  system has a metric prototype called more often the *absolute cgs* system. Here the unit of length is the *centimeter*, the unit of mass is the *gram*, and the unit of time is the *second*. The force unit, like the poundal, is expressed in derived dimensions.

$$F = ma$$

$$(1 \text{ dyne } [ML\theta^{-2}]) = (1 \text{ g } [M]) \frac{1 \text{ cm } [L]}{1 \text{ sec}^2 [\theta^2]}$$

*The dyne is defined as the force required to accelerate 1 gram mass at the rate of 1 centimeter second<sup>-2</sup>.* In using this system it must be remembered that

$$1 \text{ dyne} = 1 \frac{\text{g cm}}{\text{sec}^2}$$

<sup>1</sup> This paragraph is included because of the complexity of Table IV (Appendix)

The unit of energy in this system is called an *erg* and is defined as the product of unit force acting through unit distance

$$1 \text{ erg} = 1 \text{ dyne} \times 1 \text{ cm} = 1 \text{ dyne cm}$$

A larger unit of energy is called the *joule*

$$10^7 \text{ ergs} = 1 \text{ joule} \quad (a)$$

The unit of power, which is the energy expended in unit time, is the *watt*

$$1 \text{ watt} = 1 \frac{\text{joule}}{\text{sec}} \quad (b)$$

The measurement of basic electromagnetic quantities and the dimensions of units are based on three experimental laws *Coulomb's law* for the force action by charged bodies, *Ampère's law* for the force action between current-carrying conductors, and *Faraday's law* of induction. The units derived are theoretical or so-called *absolute* electrical units because they are related to the *cgs* system of units in mechanics.

Physically, all electromagnetic phenomena may be thought of as arising from the existence of *electric charge*, the word *charge* defining a new entity. It is known, however, that the smallest particle of matter that has ever been identified is a negative charge called an *electron*. A much larger quantity of charge is called the *coulomb* and careful measurements show that the theoretical coulomb is equivalent to  $6.2422(10)^{18}$  electrons. The displacement of charge gives rise to an electric *current* and the unit, the *ampere*, is defined as the flow of 1 coulomb of charge per second. (Conversely, from *Ampère's law* a coulomb may be defined as an ampere second.) The relationship that exists between the units permits of defining the unit of *potential*, the *volt*, in terms of energy and charge. Thus, a *potential difference* of 1 volt exists when 1 joule of energy is expended in the transfer of 1 coulomb of charge.

Since energy is expended in the transportation of electricity, a resistance to flow must be present. The unit of resistance is defined as the *ohm*. A resistance of 1 ohm exists when a potential difference of 1 volt is required for the flow of 1 ampere of current. This relationship results from *Ohm's law*.

Until recently,<sup>1</sup> for purposes of measurement and standardization an international system of electrical measurements defined the legal standards.

The *international ampere* is defined as the current that will deposit silver at the rate of 0.00111800 gram per second.

The *international ohm* is defined as the resistance at 0 degrees centigrade of a column of mercury of uniform cross section having a length 106.300 centimeters and mass 14.4521 grams.

The *international volt* is defined as the voltage that will produce a current of 1 international ampere through a resistance of 1 international ohm.

Because of these definitions, the international (int) units are slightly different in size from the theoretical or absolute units. For example, measurements show that

$$\begin{aligned} 1 \text{ international ohm} &= 1.000495 \text{ absolute ohms} \\ 1 \text{ international volt} &= 1.000330 \text{ absolute volts} \\ 1 \text{ international ampere} &= 0.999835 \text{ absolute ampere} \end{aligned}$$

<sup>1</sup> National Bureau of Standards Circular C459, May 15, 1947

**1-8. Weight.** Because the word *weight* is used in two different senses, some confusion has arisen (1) Weight is the term used to indicate the mass or quantity of matter in a body (an unfortunate usage) (2) *Weight is the force exerted on a given mass by the gravitational effect of the earth* (a better usage) When a body is "weighed" on a beam scale, it is directly balanced by a known and presumably calibrated mass, this "weighing operation" is a measure of the mass in the body because the attraction of gravity on both the known and unknown masses is equal On the other hand, when a pound mass is weighed on a spring scale, the deflection of the scale will be governed by the local value of the attraction of gravity The weight will be

$$\begin{aligned} F &= \frac{1}{g_c} ma \\ &= \frac{1}{g_c} (1 \text{ lb}_m)g \\ w &= \frac{g}{g_c} (1 \text{ lb}_m) \end{aligned}$$

(and this weight is in standard pound force units) When this method of weighing is made at a location where  $g = g_0$ , the mass of 1 pound will exert a force of 1 standard force pound (by definition) If  $g$  is greater than  $g_0$  a greater force will be exerted, and it will be so indicated if the scales have been calibrated at a region where  $g = g_0$

In most engineering work the problem of spring scales will not be a factor, but it is not unusual to use a mass as a weight For example, consider a heavy piston free to descend in a vertical cylinder filled with gas, the force exerted by the mass of the piston on the gas will vary as the location or altitude of the cylinder is varied This force in standard force pound units is

$$w = \frac{g}{g_c} m$$

where

$$w \text{ in lb}_f = \frac{g}{g_c} \times m \text{ in lb}_m$$

In some instances the gravitational force exerted by a mass of 1 pound at a location where the acceleration of gravity is  $g$  is called a *gravitational pound force* This unscientific unit must be multiplied by the ratio  $g/g_0$  if the force is to be reported in standard pound force units

Note again that a mass of 1 pound measured on a conventional beam scale is precisely 1 pound mass, but the force exerted (the weight)



is usually not 1 standard pound force because of the multiplying factor

$$\text{of } \left| \frac{g}{g_c} \right| = \left| \frac{g}{g_0} \right|$$

Throughout this text the symbol  $w$  will denote weight in standard pound units.

**1-9. Derived Dimensions and Units.** Derived or secondary dimensions will be constructed as the need for such descriptions becomes necessary

*Density* is defined as the mass contained in unit volume. The symbol for density in any units will be  $\rho$ , and dimensionally

$$[\rho] = \frac{[M]}{[L^3]} = [ML^{-3}]$$

Density is measured in units of pounds mass per cubic foot ( $\text{lb}_m/\text{ft}^3$ ) and frequently in units of slugs per cubic foot

*Specific gravity* is defined as the ratio of the density of a substance to the density of a selected reference material under prescribed conditions. The reference density is usually that of water at 39 F or at 60 F (Table III, Appendix). Note that a ratio is dimensionless.

*Specific volume*, the volume occupied by unit mass of material, is the name given to the inverse dimensions of density. The symbol of designation is  $v$ , and the dimensions of  $v$  are

$$[v] = \frac{[L^3]}{[M]} = \left[ \frac{1}{\rho} \right] = [L^3 M^{-1}]$$

Usually the engineering units are in cubic feet per pound ( $\text{ft}^3/\text{lb}_m$ )

**Example 6:** Density ( $\rho$ ) is defined as the mass contained in unit volume. Specific weight ( $\gamma$ ) is defined as the weight of the mass contained in unit volume. Investigate the relationship of these terms in the  $FML\theta$  and  $FL\theta$  systems.

**Solution:**

*FML $\theta$  System*

$$F = \frac{1}{g_c} ma$$

and

$$\gamma = \frac{1}{g_c} \rho g$$

and at locations where  $g = g_0$

$$\gamma = \frac{g_0}{g_c} \rho$$

or numerically  $\gamma$  equals  $\rho$  (at the specified location  $g = g_0$ ). This equality is convenient, for example, water at 68 F has a density of  $62.305 \text{ lb}_m/\text{ft}^3$  and weighs  $62.305 \text{ lb}/\text{ft}^3$  (unless  $g \neq g_0$ ). These units and dimensions are of everyday experience.

*FL $\theta$  System*

$$F = ma$$

$$\gamma = \rho g_0$$

under standard conditions, or numerically  $\gamma$  is 32 1739 times  $\rho$ . Using the same figures as before, the density of water in this system is

$$\rho = \frac{62\,305}{32\,1739} = 1\,936 \text{ slugs ft}^{-3} \text{ or } \left[ \frac{\text{lb}_f \text{ sec}^2}{\text{ft}^4} \right]$$

and the specific weight is

$$\gamma = 62\,305 \text{ lb}_f \text{ ft}^{-3}$$

*Viscosity* of a fluid is a measure of its resistance to shear, and thus it is a measure of the internal friction of the fluid to flow. In a *perfect fluid* the viscosity would be zero. Consider two parallel plates close together and in motion relative to each other (Fig. 1-1). Fluid in contact with the upper plate will move with

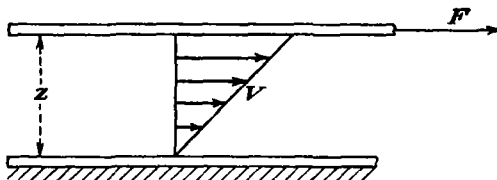


FIG. 1-1 Velocity gradient from viscosity

velocity  $V$  while fluid adhering to the lower plate will have zero velocity relative to the upper plate. Experimental tests show that the shearing stress is proportional to the velocity gradient

$$\frac{F}{A} \sim \frac{dV}{dz}$$

$$F = \mu_f A \frac{dV}{dz}$$

where  $F$  is the force applied to the plate of area  $A$  to maintain velocity  $V$  and  $\mu_f$  is a dimensional constant called the *viscosity* or *coefficient of viscosity*. Dimensionally,

$$\mu_f = \frac{[F]}{[A][dV/dz]} = \frac{[F]}{[L^2][1/\theta]} = [F\theta L^{-2}]$$

The subscript  $f$  will be used to designate force units for viscosity. In mass units

$$\mu_m = \mu_f g_c$$

$$[\mu_m] = \left[ \frac{F\theta}{L^2} \right] \left[ \frac{ML}{F\theta^2} \right] = \left[ \frac{M}{L\theta} \right]$$

Various units for viscosity are in use. Conversion factors are listed in Table I, and values of viscosity are listed in Table III (Appendix).

*Pressure* is defined as the intensity of a force and is evaluated as the force exerted on unit area. The symbol to designate pressure in any units will be  $p$  and dimensionally

$$[p] = \frac{[F]}{[A]} = [FL^{-2}]$$

The engineering unit for pressure is standard pounds of force per square inch ( $\text{lb}_f/\text{in}^2$ , or psi). In most equations, pounds per square foot will be used ( $\text{lb}_f/\text{ft}^2$ ).

The usual pressure-measuring instruments measure the pressure either above or below the atmospheric condition, and such pressures are called *gauge pressures*. The *absolute pressure* is the algebraic sum of gauge and atmospheric pressures. If a *vacuum* is reported as 28 in. of mercury with a barometric pressure of 30 in. of mercury, the absolute pressure is 2 in. of mercury. For some work the unit of pressure is taken as the *standard atmosphere*, which is defined as the pressure exerted by a column of mercury 760 millimeters in height and having a density of 13 595 grams per cubic centimeter when located in a region where the acceleration of gravity is standard

$$1 \text{ atm} = 760 \text{ mm Hg} = 29.92 \text{ in. Hg} = 14.696 \text{ psi}$$

Various pressure-measuring instruments are detailed in Table IX (Appendix) and also in Chap. IX.

**1-10. Temperature.** If a hot and a cold body are placed in contact with each other, a state of thermal equality will eventually be reached, and both bodies are then said to be at the same *temperature*. The concept of temperature is obtained from the sensation of warmth or cold experienced upon touching an object. Temperature is a fundamental<sup>1</sup> dimension and, like force, can be considered to be a potential or driving factor that can cause a change from the existing conditions. The dimension of temperature will be indicated in the usual manner by brackets and capital letter  $[T]$ . Qualitatively, it is easy to recognize a "hot" or a "cold" body, but the quantitative measurement of the degree of hotness is a difficult matter. For this reason, particular conditions of pure compounds under prescribed limitations are arbitrarily assigned a definite temperature, for then this thermal level can be readily reproduced. For such reproducible thermal states, the temperature on any arbitrary scale will be indicated by the letter  $t$ .

By international agreement, 0 degrees on the centigrade scale ( $t = 0^\circ \text{C}$ , *ice point*) is specified to be the temperature when equilibrium exists between pure ice, air, and water at a pressure of 1 atmosphere. This point corresponds to 32 degrees on the Fahrenheit scale ( $t = 32^\circ \text{F}$ ). Similarly, when pure water is in equilibrium with its vapor at a pressure of 1 atmosphere, the temperature is arbitrarily designated to be 100 degrees centigrade ( $t = 100^\circ \text{C}$ , *steam point*), and the steam point corresponds to 212 degrees Fahrenheit ( $t = 212^\circ \text{F}$ ). This procedure has determined two fixed and reproducible thermal levels, but a means must be provided to indicate any intermediate point that might be encountered, and such an indicator is called a *thermometer*. The familiar mercury-in-glass thermometer indicates temperature as related to the thermal-expansion properties of the mercury and glass. The mercury thermometer can be calibrated in an ice bath to read  $0^\circ \text{C}$  and in a steam bath to read  $100^\circ \text{C}$ , and the interval between

<sup>1</sup> The student will note that fundamental dimensions cannot be clearly explained, mass, force, time, length, and temperature are words that define things we sense to be different from each other.

these two points on the scale can be arbitrarily divided into 100 equal divisions or degrees. A reading of 38 C has no meaning, other than showing how mercury and glass expand. If a different substance from mercury were enclosed in the glass tube and this thermometer were then calibrated in the same manner, it would be unusual if this new thermometer should indicate exactly 38 C when immersed with the mercury thermometer in the supposedly 38 C medium. However, either thermometer would act as an indicator of the degree of hotness, and each in itself would reproduce a definite number when in equilibrium with a definite thermal state. Until a more rigid definition of temperature can be given (Chap V), let it be understood that the same kind of thermometer will be used for all temperature measurements in order that these measurements shall be comparable.

Many properties of materials can be used to give reproducible indications of relative thermal states. The properties commonly used are these:

- 1 Volume expansion of solids, liquids, and gases measured at constant pressure,
- 2 Pressure exerted by gases as measured at constant volume,
- 3 Electrical resistance of materials,
- 4 Vapor pressure of liquids,
- 5 Thermoelectricity

The problem is complicated by the fact that it is difficult if not impossible to select a material that will serve as a thermometer over a wide range of temperatures. The ordinary mercury-in-glass thermometer, for example, fails at the hot end of the range if only because the glass container may start to melt (900 to 1400 F) and fails at the cold end because the mercury freezes ( $-38^{\circ}\text{F}$ ).

The measurement of temperature is also discussed in Table IX (Appendix) and in Chaps V and IX.

**1-11. Dimensional Analysis.** Since a dimension describes a measurable quantity, an equation made up of dimensional terms can be visualized as a description or summation of a more complicated event. A dimensional system is invariably used to ensure that equations are dimensionally homogeneous, and a check of the correctness of an equation is to test this homogeneity. If an event is known to be dependent on certain variables, it should be possible to predict the arrangement of these variables from the principle of dimensional homogeneity of equations.

For example, consider the time of swing of a pendulum. The variables (the dimensions) describing the swing appear to be as follows:

Variables (dimensions)	Symbol	Dimensional formula
Time of swing	$\theta$	$[\theta]$
Length of pendulum	$l$	$[L]$
Mass of pendulum	$m$	$[M]$
Acceleration of gravity	$g$	$[L\theta^{-2}]$
Amplitude of swing (radians)	$\alpha$	None

To find the time of swing ( $\theta$ ) let

$$\theta = f(lmg\alpha)$$

where  $f$  is any function of these four variables. For dimensional homogeneity the dimension of  $\theta$  must be equal to that of  $f(lmg\alpha)$

$$[\theta] = [f(lmg\alpha)]$$

$$[\theta] \text{ must equal } [L][M][L\theta^{-2}]$$

Only one term involves the dimension of mass, then, this term is irrelevant, or else some other factor involving mass has been neglected. Assuming that this latter possibility is not true and dropping the mass variable,

$$[\theta] \text{ must equal } [L] \frac{[L]}{[\theta]^2}$$

To cancel the dimension of length, one term must be inverted

$$[\theta] \text{ must equal } [L] \frac{[\theta]^2}{[L]}$$

or

$$[\theta] = \left( \frac{[L][\theta]^2}{[L]} \right)^{\frac{1}{3}}$$

The answer, for dimensional homogeneity, is

$$\theta = \sqrt{\frac{l}{g}} f(\alpha)$$

where  $f(\alpha)$  must be determined experimentally

The same problem can be handled quite mechanically by the following procedure

$$[\theta] = [L]^a [M]^b [L\theta^{-2}]^c$$

Simultaneous equations can be used to solve for  $a$ ,  $b$ , and  $c$

$$\begin{array}{rclcl} \Sigma \theta & 1 & = & -2c & \text{or} & c = -\frac{1}{2} \\ \Sigma L & 0 & = & a & + c & \text{or} & a = -c = \frac{1}{2} \\ \Sigma M & 0 & = & b & & \text{or} & b = 0 \end{array}$$

Hence,  $b = 0$  and  $m$  is not a factor (or some other factor was neglected)

$$\theta = l^{\frac{1}{2}} g^{-\frac{1}{2}} f(\alpha)$$

$$\theta = \sqrt{\frac{l}{g}} f(\alpha)$$

which, of course, is the same answer as before

It should be carefully noted that dimensional analysis can do no more than systematically arrange the variables that presumably govern the event under study. If one or more of these variables is omitted, the answer found will be significant only to the degree that the missing variables are insignificant.

**Example 7:** Find an expression for the force exerted by the air on the wing of an airplane

**Solution:** The factors involved appear to be

Variables	Symbol	Dimensional formula
Area of wing	$A$	$[L^2]$
Velocity of wing	$V$	$[L\theta^{-1}]$
Density of air	$\rho$	$[ML^{-3}]$
Viscosity of air	$\mu_f$	$[F\theta L^{-2}]$
Resistance of wing	$F$	$[F]$

Since resistance of the wing is the factor to be investigated, the desired solution will have the general form

$$F = f(AV\rho\mu_fg_c)$$

where  $g_c$  must be included since the  $FLM\theta$  system is used. Dimensionally for any form of the unknown function  $f$ , the following relationship must be satisfied

$$[F] = [L^2]^a [L\theta^{-1}]^b [ML^{-3}]^c [F\theta L^{-2}]^d [MLF^{-1}\theta^{-2}]^e$$

For dimensional homogeneity the exponents of  $FLM\theta$  on both sides of the equation must be the same

$$\begin{array}{rclclcl} \Sigma F & 1 & = & & d & -e \\ \Sigma L & 0 & = & 2a + b - 3c - 2d & +e \\ \Sigma \theta & 0 & = & -b & +d & -2e \\ \Sigma M & 0 & = & & c & +e \end{array}$$

When these simultaneous equations are solved,

$$\begin{array}{ll} a = \frac{1}{2} - \frac{1}{2}e & d = 1 + e \\ b = 1 - e & e = e \\ c = -e & \end{array}$$

and the solution is

$$F = A^{\frac{1}{2}} V \mu_f f\left(\frac{\mu_f g_c}{A^{\frac{1}{2}} V \rho}\right)$$

This can be rearranged (to obtain a more familiar equation)

$$\begin{aligned} F &= A^{\frac{1}{2}} V \mu_f \left(\frac{A^{\frac{1}{2}} V \rho}{\mu_f g_c}\right) f\left(\frac{A^{\frac{1}{2}} V \rho}{\mu_f g_c}\right) \\ F &= \frac{A V^2 \rho}{g_c} f\left(\frac{A^{\frac{1}{2}} V \rho}{\mu_f g_c}\right) \quad \text{Ans} \end{aligned}$$

Upon examination of this answer, it is noticed that two dimensionless groups have been obtained

$$\left(\frac{F g_c}{A V^2 \rho}\right) \quad \text{and} \quad \left(\frac{A^{\frac{1}{2}} V \rho}{\mu_f g_c}\right)$$

The answer obtained by dimensional analysis will always contain an unknown function that must be experimentally determined. Over a limited range of variables, it is often possible to describe the experimental data with a simple exponential function. Thus, the solution to Example 7 can be premised to be

$$F = C \frac{AV^2\rho}{g_c} \left( \frac{A^\dagger V\rho}{\mu_f g_c} \right)^e$$

and this is a valid solution if values for the constant  $C$  and the exponent  $e$  can be found that will correctly evaluate the known results. (A series of terms, each with a different exponent and constant, could undoubtedly be found to describe a greater range.)

The dimensionless number,

$$\frac{A^\dagger V\rho}{\mu_f g_c} = C \left( \frac{DV\rho}{\mu_m} \right)$$

appears with great regularity whenever a dimensional analysis is made of fluid flow. In honor of Osborne Reynolds and his classic studies of fluid flow, this group has been named the *Reynolds number*. The Reynolds number is abbreviated  $Re$  and is defined

$$Re = \left( \frac{DV\rho}{\mu_m} \right) \quad (1-1)$$

Experimentally it is found that, if two different fluids in flow under apparently dissimilar conditions have the same  $Re$ , the flows are dynamically similar.

A number of rules are available to facilitate dimensional analysis:

1. *The number of dimensionless groups obtained will equal the number of factors less the number of fundamental dimensions.*
2. *If two of the simultaneous equations give the same answer, an additional dimensionless group will be obtained over the number predicted by rule 1.*
3. (a) *If the list of variables contains both  $[F]$  and  $[M]$ , the dimensional constant  $g_c$  should be included for then the answer is general for any system of dimensions (Table 1-1).* (b) *However, if the dimensions  $[F]$  and  $[M]$  both appear more than once, the constant may be superfluous.*

### Problems

1. Set up a dimensional system using as fundamental units the poundal  $[F]$ , pound  $[M]$ , foot  $[L]$ , and second  $[t]$ . What are the value and dimensions for the

dimensional constant? Eliminate the dimensional constant by giving the poundal derived dimensions, and compare the two systems Which system is used?

2. Repeat Prob 1, but use the slug  $[M]$ , pound force  $[F]$ , foot  $[L]$ , and second  $[t]$  as the fundamental units

3. A man weighs 180 lb Explain the exact meaning of this sentence

4 Explain the difference between a gravitational and a standard force pound

5. Define force pound, poundal, dyne, and erg

6 A pound mass is weighed on a beam balance at a location where  $g = 30$  ft sec<sup>-2</sup> What will be the reading? Discuss The same mass is weighed on a spring scale originally calibrated in a region where  $g \approx 32.2$  ft sec<sup>-2</sup> What will be the indicated weight? If calibration had been made at a location where  $g = 30$  ft sec<sup>-2</sup>, what would be the indicated weight and the weight in standard force pounds?

7. At a location where  $g = 30$  ft sec<sup>-2</sup>, how much mass must be used on a vertical piston to exert a force of 5 standard force pounds?

8. What is the absolute pressure in psia if (a) vacuum is 2 in Hg, (b) vacuum is 3.5 in Hg, (c) gauge pressure is 5.3 psi? (Barometric pressure is 750 mm Hg)

9 As commonly defined, 1 metric horsepower = 75 kilogram (force) meters per second. Write this in fractional form Determine

$$\left( \quad \right) \frac{\text{metric horsepower}}{\text{English horsepower}} \quad \left( \quad \right) \frac{\text{kilowatt-hours}}{\text{metric horsepower-hour}}$$

Problems 10 through 16 depend on material presented in Table IX, Appendix

10 Derive an equation for an inclined tube manometer (Fig D) that is measuring the pressure difference in a gas system of negligible density The scale reading is to be in inches of water

11 Air with density of 0.07 lb<sub>m</sub> ft<sup>-3</sup> is flowing through a pipe that is connected to a U-tube manometer in a manner similar to that shown in Fig B If the manometer depression is 3 in Hg and barometric pressure is 14.5 psi, what is the pressure in the system in pounds per square inch? (The manometer is located 10 ft below the system) Can the density of the gas be neglected? (Assume standard acceleration of gravity)

12 Repeat Prob 11, assuming that water is flowing in the pipe (Density of water is 62.3 lb<sub>m</sub> ft<sup>-3</sup>)

13 For the data of Prob 11 suppose the manometer is connected in a manner similar to Fig C and the larger static pressure is 15 psia

14 Repeat Prob 13 but with water as the fluid in flow Density is 62.3 lb<sub>m</sub> ft<sup>-3</sup>

15 Correct Probs 8 through 11 for conditions of altitude such that  $g = 28$  in Hg

16. A full-immersion thermometer is immersed in a bath to the 50 F mark The temperature shown by the thermometer is 180 F while the stem temperature is 70 F What is the true temperature of the bath?

17. Convert 60 ft sec<sup>-1</sup> to miles per hour, 1,000,000 dyne cm<sup>-2</sup> to pounds per square inch, 1,000 g cm<sup>-2</sup> to pounds per square inch, 2,000 lb<sub>f</sub> ft<sup>-2</sup> to pounds per square inch, 14 psi to atmospheres

18. Convert 500 ft lb<sub>f</sub> to horsepower-hours, 6.00(10<sup>-9</sup>) lb<sub>f</sub> hr ft<sup>-2</sup> into lb<sub>m</sub> ft<sup>-1</sup> hr<sup>-1</sup>, 100 centipoises to lb<sub>m</sub> sec<sup>-1</sup> ft<sup>-1</sup> and lb<sub>f</sub> sec ft<sup>-2</sup>



19. Convert 15 slugs to  $\text{lb}_m$ ,  $0.06 \text{ slug ft}^{-1} \text{ hr}^{-1}$  to  $\text{lb}_f \text{ ft}^{-2} \text{ hr}$ , 50 poises to  $\text{slug ft}^{-1} \text{ hr}^{-1}$

20. A 15  $\text{lb}_m$  is contained in a volume of  $\frac{1}{2} \text{ ft}^3$ . Determine the density, specific volume, and specific gravity. (Specific volume of water at 39 F is  $0.01602 \text{ ft}^3 \text{ lb}_m^{-1}$ .)

21. A cylindrical tank 10 ft in length and 3 ft in diameter contains 5  $\text{lb}_m$  of fluid. Determine the specific volume and the density of the fluid.

22. Convert  $-40^\circ \text{C}$  to Fahrenheit;  $39^\circ \text{C}$  to Fahrenheit,  $100^\circ \text{F}$  to centigrade.

23. Define what is meant by a reproducible thermal state and give several familiar examples.

24. Determine by dimensional analysis the form of the equation in the engineering  $FL\theta$  system for the velocity of sound in a gas if the variables are velocity, density, and pressure of the gas.

25. Repeat Prob. 24, but use the  $FL\theta$  system.

26. Show that the pressure gradient for liquid flowing in a pipe is given by

$$\frac{\Delta p}{\Delta L} = \frac{\rho V}{Dg_c} f \left( \frac{\mu_m}{DV\rho} \right)$$

where  $D$  is the diameter and  $L$  is the length of the pipe.

27. Air is flowing through a pipe of 1.820 in. diameter at a rate of  $1.173 \text{ lb}_m \text{ sec}^{-1}$ . The temperature of the air is  $60^\circ \text{F}$ . Determine the value for  $Re$ . (Use Table III, Appendix.) Ans. 815,000

### Symbols

$a$	acceleration
$A$	area
$C$	constant
$C$	centigrade scale of temperature
$D$	diameter
$e$	unknown exponent
$f$	function
$F$	force
$F$	Fahrenheit scale of temperature
$G$	specific gravity
$g$	gram
$g$	local acceleration of gravity
$g_0$	standard acceleration of gravity
$g_c$	dimensional constant for any system
$l, L$	length
$m$	mass, also, mass flow rate
$M$	mass dimension
$p$	pressure
$t$	temperature on any reproducible scale
$v$	specific volume
$V$	velocity, also, volume
$w$	gravitational force or weight in standard force pound units
$z$	height, distance
$\sim$	proportional sign
$[ ]$	dimension
$   $	numerical equality
$\approx$	approaching equality

**Subscripts**

<i>c</i>	constant
<i>f</i>	force or force units
<i>m</i>	mass or mass units

**Abbreviations**

atm	atmosphere
cm	centimeter
ft	foot
Hg	mercury
hr	hour
in.	inch
lb	pound
mm	millimeters
mph	miles per hour
psi	pounds force per square inch
<i>Re</i>	Reynolds number
sec	second

**Greek Letters**

$\alpha$	(alpha)	angle in radians
$\gamma$	(gamma)	specific weight
$\theta$	(theta)	time
$\mu$	(mu)	viscosity
$\rho$	(rho)	density

**Suggested References**

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## CHAPTER II

### FUNDAMENTAL CONCEPTS

It is necessary in any subject of study to define the fundamental concepts rigorously, for these definitions lay the foundation for a workable theory. From experience it has been found that the definitions in this chapter are indispensable in the analysis of thermodynamic problems. For this reason, they must be thoroughly understood and remembered by the student.

**2-1. Energy.** Energy is broadly defined as the ability to produce a change from the existing conditions. Thus, the term *energy* implies that a capacity for action is present. The presence of energy is signified by many factors, for all matter has or contains latent or discernible amounts of energy in many forms. Although the absolute evaluation of energy may prove to be a difficult if not an impossible task, the relative amount of energy contained or associated with matter can be evaluated. This evaluation is done by measuring certain effects that are classified by descriptive names, and these effects can be produced under controlled conditions. For example, a mass possesses *potential energy*, or energy of position, when the mass is located above the lowest surface of the earth that will be encountered. Here the gravitational attraction of the earth on the mass can be utilized as a source of energy. When a mass is in motion, it possesses *kinetic energy*, for by changing the velocity an effect can be produced while the kinetic energy is proportionately changed. Kinetic energy, then, is energy that is available because of the mass and the velocity of a body. Both kinetic and potential energy are *external* forms of energy that are evaluated without regard to possible changes in the composition or characteristics of the mass.

The presence of another form of energy is evident by changes in characteristics or composition of the mass under observation, and therefore this form of energy is called *internal energy*. All matter contains internal energy in chemical and molecular forms (and also in atomic form). Consider a mixture of air and gasoline vapor held under pressure and confined by a piston in a horizontal cylinder. Here the piston is connected by some means to an external load that

will be lifted when the mixture is allowed to expand. Examination of the mixture before and after the expansion would show no change in composition but a definite change in characteristics such as pressure and temperature. *Internal energy* has been released of an amount that can be measured by the change in potential energy experienced by the external load. A greater load can be displaced if, in the above mechanism, a spark is used to ignite the gas-air mixture. In this instance an additional amount of internal energy is released because of a chemical reaction between the air and gasoline vapor, and a change in the composition of the mixture has occurred. The term *internal energy* is used to include all forms of energy contained within the mass whether or not a chemical change must occur to release it. (Atomic research reveals that mass and energy are fundamentally the same type of thing and are mutually convertible, although, as yet, this conversion need not enter engineering calculations.)

Dimensionally, the defining equation for energy is stated in terms of the change that can be measured when energy is transformed. One of man's earliest observations was that the simplest changes required a force to be exerted through a distance and that the product of force times distance was proportional to the effort expended. Thus, energy is defined

$$[E] = [LF]$$

Energy in general—that is, in all forms—will be designated by the letter  $E$ , with the lower-case letter  $e$  used for the quantity of energy associated with unit mass. Note that energy is evaluated as a relative and not as an absolute value because only the change in energy can be conveniently measured. It is always possible to select a datum or reference condition that can be arbitrarily assigned a value of zero energy while the determination of the absolute quantity might well prove impossible.

*Power* is defined as the time rate of energy expenditure

$$[\text{Power}] = [P] = \frac{[E]}{[\theta]} = \frac{[LF]}{[\theta]} = [LF\theta^{-1}]$$

**2-2. The System.** Before a change can be analyzed, it is essential that the participants, mass and energy, be known and included in the analysis. To ensure that this requirement is met,

**the system is defined as the region where transfers of mass and energy are to be studied.**

Since both mass and energy may be added to the system, an especially important concept is the boundary to the system, called the *system line*, or, simply, the *boundary*. All mass and energy transfers are evaluated at the boundary. The boundary may be either elastic or fixed, depending on whether or not the system is allowed to expand.

**The region outside the system is called the surroundings.**

Two general types of systems will be encountered, *closed* and *open* systems. A *closed system* contains a constant mass, and only energy is allowed to cross the boundary. In Art. 2-1, energy was obtained from a fluid enclosed in a cylinder, this is a *closed* or *nonflow* system because mass was not transferred across the boundary. An *open system* has a mass flow either into or out of the system, or both, and the mass within the system may or may not vary in amount with time. The open system is characterized by such transfers of mass across the boundary, although transfer of energy may also occur. For example, a water wheel is suspended in a channel of moving water, and the boundaries of this open system are established to enclose the wheel and adjacent parts of the channel. Here a mass flow crosses the boundary at two locations while energy alone is transferred at yet another location (and the mass within the system is a constant quantity). The moving wheel, which is *in the system*, transfers the energy for a load, which is *in the surroundings*.

In establishing a system boundary, a practical difficulty arises. Should the boundary include or exclude the structural members necessary to perform an experiment? Consider, as an example, a tank containing compressed air. This is a closed system with fixed boundaries. If the object of the study were to observe how the characteristics of the confined air changed under different conditions, then the desired system should consist of air alone with the boundary defined as the envelope of the fluid. The fluid would be the system, and the tank would be a part of the surroundings. In the laboratory, however, the effect of the container on the enclosed fluid could not be ignored, and the system under observation must include both gas and tank.

Whenever possible, the word *system* will be used to denote only the mass whose characteristics are to be observed, and the *boundaries* of this system will mark the extent of the *region* that the mass occupies. All structural parts necessary to enclose this system can be imagined as quite small, so that in the limit the mass of such parts will approach zero.



**2-3. Property, State, and Process.** After the system has been established, different conditions will be recognizable. A closed system of gas would have a definite pressure, temperature, volume, and color and would exhibit other characteristics at any stage of an experiment. All such characteristics are dimensions of the system. If a dimension is reproducible, it is called a *property* of the system. That is, if a series of changes occurs until finally the original condition is restored, a *property* will regain its original value or indication (of pressure, temperature, volume, etc.). The condition, or *state*, of the system can be identified by the properties.

**A property is a function of the state (a point function) and depends only on the state and not on the method of change between two states.**

Since a property helps to identify a particular state, the change in value of a property between any two states does not depend on the *process*.

**A process occurs whenever the system changes from one state to another state.**

*Intensive* properties or *potentials* are independent of the extent of the system, as, for example, pressure, temperature, electrical potential, velocity, surface tension, and height. These potentials are the driving factors that can cause a change in state. *Extensive* properties, such as energy, volume, and area, depend on the extent of the system. *Specific* values of extensive properties, that is, values per unit mass, are considered to be *intensive* properties: specific volume ( $\text{ft}^3 \text{lb}_m^{-1}$ ), specific internal energy ( $\text{Btu lb}_m^{-1}$ ), etc. Although in following pages specific values are most often implied, the word *specific* will not always be used (except, invariably, for specific volume).

A system is in *equilibrium* when it is incapable of spontaneous change, that is, change without help from some external agency. Since a process passes through an infinite series of states, each of which is identified by properties, it follows that a process must proceed at an infinitely slow speed if each state attained is to be an equilibrium state, which is a state of *constancy*.

**2-4. Phases and Components.** A quantity of matter that is homogeneous throughout in chemical and physical composition is called a *phase*. Homogeneity in the thermodynamic sense does not imply a single molecular species, for a mixture of gases or a solution is a *phase*. If oxygen and hydrogen are mixed together, the resulting gas phase has two *components*, hydrogen and oxygen. Similarly, alcohol

and water will mix to form a single liquid phase of two components. On the other hand, water and gasoline are not miscible but, rather, will form two liquid phases, each of one component. A phase may exist in either the gaseous, liquid, or solid form.

A system comprising a single phase is called a *homogeneous* system, while a *heterogeneous* system consists of more than one phase. The number of components in either of these systems can be one or more than one.

**2-5. Definition of the State.** The properties of the system identify the state, and, conversely, once the state is defined, all the properties assume definite values although these values are not necessarily known. The number of properties necessary to define the state will vary, *for the simplest system, two independent intensive properties will suffice.* An *independent property*, as the name implies, is one that does not depend on the value of another property. For example, water under 1 atm pressure can be heated from the freezing point to the boiling point. The properties of pressure and temperature are *independent* of each other within this range and together determine the state. When boiling begins and two phases appear, the properties of pressure and temperature are no longer independent but *dependent* upon each other, for one cannot be changed without changing the other. The state must then be defined by either temperature or pressure and one other independent property, for example, specific volume. When the liquid phase is vaporized, only a gaseous phase remains. The state of this phase can then be determined by the properties of temperature and pressure, which once more are independent of each other.

Thus, a change in state may be signaled by a change in the properties of pressure and temperature, and these properties can be conveniently measured. A datum state can be selected and assigned a value of zero specific internal energy. Now by measurements of the energy that must be transferred to change the state from this datum, it is possible to evaluate the internal energy at each higher state of energy (or, at least, the relative value of this property to the datum state). In this manner, tables of data can be compiled for the fluids in common use, the properties of pressure and temperature (or specific volume) serving as the parameters for tabulating internal energy.

Suppose that water is flowing through a pipe and the independent properties of pressure and temperature are measured. These properties are adequate to define the state of a quiescent fluid, but here the fluid is in motion. In this case the velocity must also be measured, for velocity is a property that specifies the specific kinetic energy.

that the fluid possesses. Thus, for this system three independent properties are required to define the state. In similar manner, if the fluid in its passage through the pipe experiences a difference in elevation, a change of state has occurred because the potential energy of the fluid has changed. The state of the fluid at any instant is defined by the four independent properties of pressure, temperature, velocity, and elevation. Any or all of these properties may continuously change as the fluid passes through the pipe. Here it should be noted that the properties of pressure and temperature are an independent measure of the internal energy of the fluid, the property of velocity is an independent measure of the kinetic energy of the fluid, and the property of elevation is an independent measure of the potential energy of the fluid. The state of the system is simply the energy state described by these independent properties. Each form of energy can be superimposed upon the others, and, for this reason, measurements of "internal" properties, such as temperature and pressure, enable the internal energy to be determined from data originally compiled from tests made on quiescent fluids. And measurements of "external" properties, such as velocity and elevation, enable the specific values of kinetic energy and potential energy to be determined as quite independent forms of energy.

**2-6. Heat and Work.** If two copper blocks are placed together, and one block is hotter than the other, the temperatures of the blocks will change. If one of the blocks is defined to be the system under scrutiny (and the other block is the surroundings), it is evident that internal energy is being transferred across the boundary of the system. The condition necessary for this transfer of energy is the temperature difference between the system (one block) and its surroundings (the second block).

**Heat is energy transferred, without transfer of mass, across the boundary of a system because of a temperature difference between system and surroundings.**

Consider the system to be made up of two blocks, one hot and one cold. Is the term *heat* applicable to this situation? No, because the energy within this system is constant. Energy passes from the hot to the cold block, but no energy crosses the system boundary. No temperature differential exists across the boundary.

Heat, then, is technically a term reserved for transfers of energy where the driving factor (potential) is a temperature difference *across a system boundary*. It is wrong under this definition to speak of heat

contained in a body, the correct term is *internal energy* in a body. Note, too, that heat can be identified only in reference to a system line.

Work, like heat, is transitional in nature and cannot be stored in mass or in a system. Work exists or occurs only during a transfer of energy into or out of a system and, like heat, is evidenced by a change in the surroundings. After the work is done no work is present, only the result of the work—energy. A definition for work can be made by paraphrasing the definition for heat:

**Work is energy transferred, without transfer of mass, across the boundary of a system because of an intensive property difference other than temperature that exists between system and surroundings.**

The usual intensive property encountered in heat-power work is pressure, although energy transferred by electrical means would also be work, and here the intensive property would be electrical potential (emf).

The symbols for heat and work will be  $Q$  and  $W$ , and the dimension that of energy. Although heat, work, and energy have the same dimension, only energy is a property identifying the state of a system. Heat and work are not properties because they appear only when a change of state occurs and disappear when the process is completed.

**2-7. Conduction, Radiation, and Convection.** Energy, in response to a temperature difference, is transferred by two methods, called *conduction* and *radiation*. When *conduction* of energy occurs, a mass is the medium between the high- and low-temperature regions that serves as a conductor for the transfer of energy. If one end of a metal rod is thrust into a fire, the other end will gradually become hot; internal energy is transferred from the hotter end by conduction to the colder end. Similarly, two masses, one hot and one cold, when placed together will transfer energy by conduction.

All bodies lose energy continuously by *radiation*. Radiation can be pictured as a shower of small discrete “bullets” of energy projected with the velocity of light. The transfer of energy by radiation requires no intervening medium or conductor for the energy. Energy is continuously radiated from all bodies. A body that is hot relative to its surroundings radiates more energy than it receives, while its surroundings absorb more energy than they radiate. The net exchange of radiation is a transfer of energy through a temperature difference.

When energy is transferred from a hot to a cold body by mass movement of a fluid, the method is called *convection*. A house can be heated by passing air over a hot surface in a furnace to receive energy by conduction, then by passing it over the walls of the house to transfer energy again by conduction. *Convection* can be defined as double conduction distinguished by the presence of a fluid *carrier*. When a fluid is heated, it becomes less dense and may be displaced by colder fluid. Movement of the carrier by this method is called *natural* or *free convection*. When the carrier is forced to move by means of a pump or fan, the method is called *forced convection*.

Combinations of these modes of energy transfer are quite common. For example, when two masses *in vacuo* are moving toward each other, energy is transferred by radiation. At the instant before contact only radiation is involved, but, during contact, energy is transferred by conduction and radiation. Similarly, the exterior walls of a furnace radiate some energy while the carrier (air) bears further energy to the surroundings by convection.

Whether or not the term *heat* can be applied to these energy transfers rests entirely upon the definition of the system and, therefore, upon the location of the boundary. However, in technical literature the word *heat* is often used whenever thermal effects are present without regard for the more precise thermodynamic meaning discussed in Art 2-6.

**2-8. Units and Measurement of Work and Heat.** In mechanical engineering the usual intensive factor causing a transfer of energy in the form of work is pressure, pressure multiplied by the area exposed to the pressure is force, and the product of force and the distance of application of the force has dimensions of energy. Accordingly, *mechanical work* is measured in the dimensions already prescribed for energy

$$[W] = [p][A][L] = \frac{[F]}{[A]} [A][L] = [LF]$$

The historic experiment in 1840 of J. P. Joule showed that churning water by paddles and thus dissipating mechanical work could warm the water and bring about the same result that could be accomplished by transfer of heat. In this way the relationship between heat and work was determined. Since most of the early experiments were intimately involved with the thermal properties of water, an energy unit was defined in terms of water. This energy unit (as well as a slightly smaller unit now in use) is called the *British thermal unit*

(*Btu*) In terms of water, the *mean Btu* is defined as  $\frac{1}{180}$  of the energy required to raise the temperature of 1 pound mass of water from 32 to 212 F—through 180 degrees. The corresponding unit in the metric (cgs) system is called the *mean calorie* (cal) and equals  $\frac{1}{180}$  of the energy required to raise the temperature of 1 gram mass of water from 0 to 100 C. One *kilocalorie* or *kilogram-calorie* equals 1000 calories. Obviously, a basic energy unit need not be bound to water, and at the *International Steam Table Conference* in 1929 it was agreed arbitrarily to fix the unit in terms of basic international electric-energy units<sup>1</sup>. This resulting unit, called the *International Steam Table calorie* (IT cal) is defined as follows

$$1000 \text{ IT cal} = \frac{1}{860} \text{ int kwhr}$$

The Btu in use today by engineers<sup>2</sup> is defined in terms of the IT calorie

$$1 \frac{\text{IT Btu}}{^{\circ}\text{F lb}_m} = 1 \frac{\text{IT cal}}{^{\circ}\text{C g}}$$

In words, 1 IT Btu will raise 1 pound of mass 1 degree Fahrenheit if 1 IT calorie will raise 1 gram of the same mass 1 degree centigrade. It follows that

$$\begin{aligned} 1 \text{ IT Btu} &= 251.996 \text{ IT cal} \\ 1 \text{ int kwhr} &= 3412.76 \text{ IT Btu} \end{aligned}$$

In the following pages, the abbreviation *Btu* without the prefix *IT* is understood to be that defined in terms of the international calorie.

The dimensional constant that relates the thermal units to the mechanical units is called the *mechanical equivalent J* or *Joule's equivalent*<sup>3</sup>. Such a constant can always be shown as a unit conversion factor (Art 1-6)

$$\begin{aligned} J &= 778.16 \frac{\text{ft lb}_f}{\text{Btu}} \\ 1 \text{ Btu} &= 778.16 \text{ ft lb}_f \end{aligned}$$

Since thermodynamic equations are homogeneous, each term can be measured in the same units, and therefore *J* is not a necessary part of the equations. However, certain properties are invariably expressed in certain units: internal energy in thermal units, kinetic and potential energy in mechanical units. In equations containing these combina-

<sup>1</sup> Table IV, Appendix, and Art 1-7

<sup>2</sup> In thermochemistry, the *defined Btu* is used (Table IV, Appendix)

<sup>3</sup> Table IV, Appendix

tions,  $J$  will be included for the convenience of the student. In equations that do not involve kinetic or potential energy,  $J$  may not be included

Electrical work, like mechanical work, is measured as the product of an intensive factor and an extensive factor. Here the intensive property can be considered to be the *potential difference* (emf), which will be designated by the symbol  $\varepsilon$ . The extensive factor is the *quantity* (or *charge*) of electricity that flows through the potential difference. Accordingly, the work is

$$W = \varepsilon q$$

and the units are

$$(\text{Joules}) = (\text{volts})(\text{coulombs})$$

The rate of flow of electricity is called the *current*  $i$  where

$$i = \frac{\text{quantity}}{\text{time}} = \frac{q}{\theta}$$

with units

$$\text{Amperes} = \frac{\text{coulombs}}{\text{seconds}}$$

Hence,

$$W = \varepsilon i \theta$$

Power is defined

$$P = \frac{W}{\theta} \\ = \varepsilon i$$

and the units are

$$(\text{Watts}) = (\text{volts})(\text{amperes})$$

Conversion factors for these electrical units are given in Table I, Appendix

The engineering dimensional system need not be expanded to include heat and work as separate and distinct fundamental dimensions because both of these effects can be expressed as derived dimensions

$$[\text{Work or heat}] = [\text{ft lb}_f]$$

However, for convenience, heat may be considered to be a basic dimension, and a dimensional system based on five fundamental dimensions can be used

$$[L][\theta][M][F][H] \quad (\text{five fundamental dimensions})$$

Temperature is another fundamental dimension that can be included in the dimensional system. In this case, a six-fundamental-dimension system will result

$$[T][L][\theta][M][F][H] \quad (\text{six fundamental dimensions})$$

**2-9. Dimensions and Units for Energy.** *Potential Energy* Potential energy is restricted to gravitational energy, that is, energy that can be realized by changing the position of a mass with respect to the surface of the earth. The dimension of potential energy must be the same as that assigned to energy

PE = potential energy = gravitational force  $\times$  height

$$PE = wz = m \frac{g}{g_c} z \quad (2-1)$$

$$[PE] = [LF]$$

Before potential energy can be calculated, a plane of zero potential energy must be assumed, and it is usual to take the lowest elevation that will be encountered as this datum. From this plane the height of the mass is determined, and the potential energy relative to this datum is calculated.

**Example 1.** Calculate the potential energy of 32 1739 lb<sub>m</sub> at an elevation of 100 ft above an arbitrary datum of zero potential energy.

**Solution.** From the *FMLθ* system,

Potential energy PE = (gravitational force *w*)(height *z*)

$$\begin{aligned} PE &= wz = m \frac{g}{g_c} z \\ &= (32\,1739 \text{ lb}_m) \frac{g}{g_c} (100 \text{ ft}) \\ &= 3,217\,39 \frac{g}{g_0} \text{ ft lb}_f \quad \text{Ans} \end{aligned}$$

Checking the dimensions,

$$\begin{aligned} PE &= m \frac{g}{g_c} z \\ [PE] &= [M] \left[ \frac{\frac{L}{\theta^2}}{\frac{ML}{F\theta^2}} \right] [L] = [LF] \end{aligned}$$

and this is the correct dimension. In some cases *mz* is incorrectly taken to be the measure of potential energy

$$PE = mz = 32\,1739(100) = 3,217\,39 \text{ ft lb}_m$$

and this is numerically correct if  $g/g_0 = 1.0$  but dimensionally wrong because ft lb<sub>m</sub> is not the dimension for energy.

From the *FLθ* system,

$$PE = wz = mgz$$

where *m* is in slugs

$$PE = 100g \text{ ft slug} \quad \text{Ans}$$

That the answer in the correct units can be seen by substituting

$$1 \text{ slug} = \frac{1 \text{ lb}_f \text{ sec}^2}{\text{ft}}$$

and

$$\begin{aligned} PE &= 100g \text{ lb}_f \text{ sec}^2 \\ &= 3,217\,39 \frac{g}{g_0} \text{ ft lb}_f \end{aligned}$$



**Kinetic Energy** Kinetic energy is energy that is available because of the mass and velocity of a body, and it must have the dimension assigned previously to energy in general, that is,  $[LF]$ . To determine the dimensional equation for kinetic energy, consider a ball held *in vacuo* at an elevation  $z$  ft above some datum plane. The ball relative to the datum has  $wz$  ft lb<sub>f</sub> of potential energy and zero kinetic energy. If the ball is allowed to fall, at the instant it reaches the datum plane its potential energy is zero but its kinetic energy is greater than zero. Since no other changes have occurred, the gain in kinetic energy is equal to the loss in potential energy. It is required in this case that

$$PE = KE$$

$$\text{Final velocity } V = g\theta$$

$$\text{Average velocity } V_{\text{avg}} = \frac{1}{2}g\theta = \frac{1}{2}V$$

Hence,

$$z = V_{\text{avg}}\theta = \frac{1}{2}V\theta$$

$$PE = KE = wz = m \frac{g}{g_c} z$$

When the equivalent  $\frac{1}{2}V\theta$  is substituted for  $z$ ,

$$KE = m \frac{g}{g_c} \left( \frac{1}{2} V\theta \right)$$

But  $g\theta$  is the velocity  $V$ , hence,

$$KE = \frac{1}{2} \frac{m}{g_c} V^2 \quad (2-2)$$

$$[KE] = [LF]$$

and this is the defining equation for kinetic energy

Kinetic energy, like potential energy, is a relative term. In measuring potential energies, a datum plane has to be selected for each problem. In measuring kinetic energy the datum must also be selected, it is usually automatically selected by measuring velocities relative to the earth.

**Example 2.** The equation for kinetic energy was found to be  $\frac{1}{2}(m/g_c)V^2$ . Show that this equation has the proper dimensions for an energy quantity.

**Solution.**

$$KE = \frac{1}{2} \frac{m}{g_c} V^2$$

$$[KE] = \left[ \frac{[M]}{[FL^{-1}]} \right] \left[ \frac{[L]}{[\theta]} \right]^2 = [LF]$$

In some instances the equation is written with  $g$  as the divisor:

$$KE = \frac{1}{2} \frac{m}{g} V^2$$

$$[KE] = \left[ \frac{[M]}{\frac{[L]}{[g^2]}} \right] \left[ \frac{[L]}{[\theta]} \right]^2 = [LM]$$

and for conditions such that  $g = g_0$ , this equation will give numerically correct results for  $m$  in pounds mass and  $V$  in feet per second, but it is dimensionally wrong because  $[LM]$  is not the dimension of energy

In the  $FL\theta$  system,

$$KE = \frac{1}{2} m V^2$$

where  $m$  = slugs with dimension  $\left[ \frac{F\theta^2}{L} \right]$

$$[KE] = \frac{1}{2} \left[ \frac{F\theta^2}{L} \right] \left[ \frac{[L]}{[\theta]} \right]^2 = [LF]$$

and this is the correct dimension (correct numerical result for  $m$  in slugs and  $V$  in feet per second)

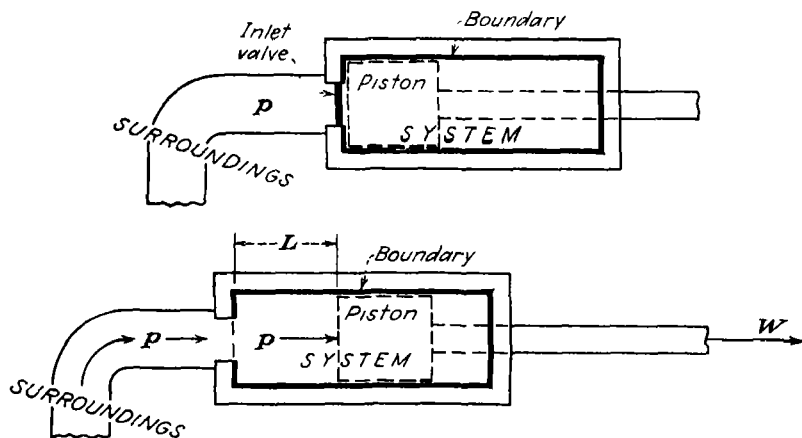


FIG 2-1 Open system with mass crossing the boundary line

**Flow Energy** An open system has transfers of mass as well as of energy between system and surroundings, and because of the mass transfer, a new form of energy must be recognized. Consider the cylinder of Fig 2-1 to be the region and also the boundary for an open system. Suppose the inlet valve is opened and fluid enters the system, pushing the piston a distance  $L$ . If this operation is slowly performed, the pressure of the fluid will remain essentially constant and the state of the fluid will not change during the process. But work has been

done by the system because the piston is connected to some external load, and this work has been done with no change in energy of the fluid. Obviously, the energy used to accomplish this work was transmitted

from a pump somewhere in the surroundings that forced the fluid into the system. In recognition of this energy that accompanies flow, the fluid is considered to have not only internal energy but also *flow energy*. With fluid flow, the energy entering the system will consist of *potential, kinetic, internal, and flow energy*.

Flow energy can be evaluated by noting the work that must be done to force each particle of mass across the boundary of the system. In Fig 2-2 a small amount of mass  $\delta m$  is entering an open system. This mass will have definite amounts of kinetic, potential, and internal energy. Now if the mass is to enter the system *without change in these forms of energy*, the surroundings must exert a force of  $pA$  to push the mass into the system. The work done by the surroundings will be

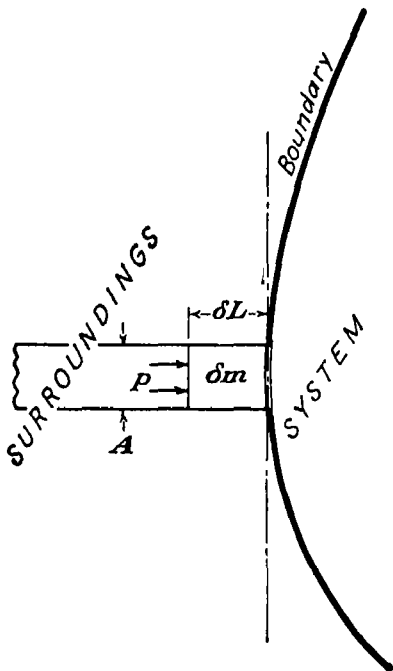


FIG 2-2 General open system (The boundary is an imaginary surface that separates the system from the surroundings)

$$\delta W = pA\delta L \text{ ft lb}_f$$

But  $A\delta L$  is the volume  $\delta V$  of the mass  $\delta m$ , and therefore the work is

$$\delta W = p\delta V$$

and for unit mass

$$W = pv \frac{\text{ft lb}_f}{\text{lb}_m}$$

where  $v$  is the specific volume of the fluid

Whenever unit mass enters a system with no change in properties, the energy content of the system is increased by the amount  $pv$  and by the kinetic, potential, and internal energy of the unit mass. When a fluid flows into the system of Fig 2-2 (or Fig 2-1), the force  $pA$  on

each mass of fluid  $\delta m$  is exerted by fluid following  $\delta m$ , and this fluid in turn will enter the system. As each element of fluid enters the system, it carries with it, as a consequence of its entry, the energy  $pv$ , which will be called *flow energy*. Whether  $pv$  is to be called *flow work*, which is done *on* the system or *flow energy* that is carried *into* the system, depends entirely on the viewpoint of the observer. To an observer measuring the change in energy within the system,  $pv$  is properly called *flow work*. To an observer evaluating the energy of a fluid flow at the boundary of a system,  $pv$  is better named *flow energy*. Note that the flow energy is entirely independent of the kinetic energy, which in many cases approaches zero. Note, too, that for conditions of no flow, energy of flow (*flow energy*) must *by definition* be zero although the product  $pv$  is not zero.

$$\text{FE} = pv \frac{\text{ft lb}_f}{\text{lb}_m} \quad \text{and} \quad \frac{pv}{J} = \frac{\text{Btu}}{\text{lb}_m} \quad (2-3)$$

**2-10. Energy in General.** Although the forms of energy are many and varied, in mechanical engineering only internal, flow, kinetic, and potential energy are of significant importance. The symbol  $E$  is the all-inclusive designation of energy, and by definition

Energy in general = internal + flow + kinetic + potential + others

$$\begin{aligned} E &= U + \text{FE} + \text{KE} + \text{PE} + \text{etc} \\ E &= U + m \frac{pv}{J} + \frac{mV^2}{2Jg_c} + \frac{wz}{J} + \text{etc} \end{aligned} \quad (2-4)$$

and, the specific values for unit mass,

$$e = u + \frac{pv}{J} + \frac{V^2}{2Jg_c} + \frac{g}{Jg_c} z + \text{etc} \quad (2-5)$$

Although each of these terms is calculated from assumed and different data, a difference in energy is the measured quantity, and, in most cases, data locations will cancel.

Equations (2-4) and (2-5) must be used with care, for all of these forms of energy may not be present. Consider, for example, an insulated tank of stagnant gas. Examination will show that the energy of the gas must be entirely in the form of internal energy because no flow or velocity<sup>1</sup> is present. Suppose that an additional quantity of gas is pumped into the tank. An observer stationed within the tank would note only that the gas is being compressed with consequent rise in temperature, and therefore the internal energy is being increased.

<sup>1</sup> Potential energy is here assumed to be negligible.

After the pumping operation is stopped, examination would reveal that the mass and the internal energy of the gas in the tank have been increased. The energy<sup>1</sup> added to the system is found by the observer to be

$$\Delta E = \Delta U = m_2 u_2 - m_1 u_1$$

Subscript 2 refers to conditions in the tank at the end of the process. Subscript 1 refers to conditions in tank at the beginning of the process.

Suppose that a second observer is stationed at the boundary of this system during the pumping operation. He would note that a mass flow of fluid is entering the system and that each element of mass has associated with it a definite quantity of internal, flow, and kinetic energy. The energy<sup>1</sup> added to the system would be evaluated by this observer as

$$\Delta E = \sum m_{\text{flow}} \left( u + \frac{pv}{J} + \frac{V^2}{2Jg_c} \right)$$

and, of course, this increase in energy must be exactly equal to that found by the first observer. Note that, while many forms of energy entered the system, all these forms were finally transformed into internal energy.

In a similar manner, suppose a discharge valve on the tank is opened. An observer stationed within the system would note only that the gas is expanding and the temperature is falling, and therefore the internal energy is decreasing. But an observer stationed at the discharge boundary of the system would note a mass flow of fluid crossing the boundary and, because of this flow, internal, flow, and kinetic energy leaving the system. In this case internal energy has been transformed, in part, into flow and kinetic energy; and the decrease in energy of the system is equal, as before, to the sum of the energies leaving the system.

These examples illustrate that, for a reservoir of fluid in the absence of flow, the energy of the system will be primarily in the form of internal energy, although the product  $pv$  will not be zero. The product  $pv$  is an energy term only at a location where mass transfer is present, and then, somewhere, other forms of energy are the ultimate sources of the flow energy. For this reason flow energy can never be stored, as such, in a system, and in this respect flow energy differs from the other forms of energy (and resembles work).

<sup>1</sup> Note Art. 9-19

It would, theoretically, be possible for a velocity to exist within a closed system, such as a reservoir of gas, and in this case the energy stored in the system would consist of internal and also kinetic energy (and flow energy would be zero since no mass is transferred across the boundary). Similarly, a reservoir of fluid possesses potential energy, and the potential energy is evaluated without regard for the evaluation of internal energy. It follows that kinetic, potential, and internal energy are basic forms of energy that can be stored in a system quite independently of each other. Flow energy is derived from these other forms of energy and cannot be stored in a system, although it can be evaluated as a separate form of energy whenever a mass flow is entering or leaving a system.

**2-11. Enthalpy.** A system has many properties that aid in identifying the state. Since in some processes many of these properties appear in a definite grouping, it may be convenient to define new properties in terms of the simpler properties. *Enthalpy*  $h$  is such a composite term, and it is arbitrarily defined as the sum of the internal energy  $u$  and the product  $pv$

$$h = u + pv \quad (2-6a)$$

Since enthalpy is invariably measured in thermal units, Eq. (2-6a) will most often be written

$$h = u + \frac{pv}{J} \quad (2-6b)$$

Since  $u$ ,  $p$ , and  $v$  are all properties, then  $h$  must be a property. The combination of terms constituting enthalpy makes its use particularly significant in processes involving open systems. Thus, whenever a mass flow crosses the boundary of a system, for simplicity the symbol  $h$  can be substituted for the combination of  $u + pv$  (the internal plus the flow energy) in evaluating the energy of flow.

**Example 3:** A fluid in flow has an internal energy of  $100 \text{ Btu lb}_m^{-1}$ , a pressure of 100 psia and a specific volume of  $5 \text{ ft}^3$ . What is the enthalpy of unit mass of fluid?

**Solution:** By definition,

$$\begin{aligned} h &= u + \frac{pv}{J} \\ &= 100 \frac{\text{Btu}}{\text{lb}_m} + \frac{(100 \text{ lb}_f/\text{in}^2)(144 \text{ in}^2/\text{ft}^2)(5 \text{ ft}^3/\text{lb}_m)}{(778.16 \text{ ft lb}_f/\text{Btu})} \\ &= 100 + 92.5 \\ &= 192.5 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

## Problems

1. Will there be an open or a closed system in the operation of the following equipment? Explain and show diagrammatic sketch of system and boundary

- |  |   |
|--|---|
| a Water pump   | f Automobile engine   |
| b Pressure cooker  | g Steam boiler in house, including all piping and radiators       |
| c Water wheel  | h A dashpot consisting of a cylinder, piston, and contained fluid |
| d Thermometer (entire system) surrounded by a medium at a higher temperature | i An ice-cream freezer (manual crank operation)                   |
| e A baseball in flight   |   |

List the substances or materials making up the system

2. State whether heat or work crosses the boundaries of the systems of Prob 1, and for heat transfers differentiate between radiation, conduction, and convection

3. For each system of Prob 1 identify the kind of energy that is contained or transferred in the process

4. For each of the following systems subjected to the specified process explain (1) whether it is an open or closed system, (2) the nature and algebraic sign of the heat or work transfers, (3) the nature and sign of the change in internal energy. The system is defined by the words in *italics*

a A perfectly insulated rigid *container* containing *air* and an electric *heating element* that is connected to an external source of power. The temperature and pressure of the air are rising

b The same apparatus as in (a) above except that the system includes only the *air*

c A small pile of *coal* and the *air* in a large, rigid container, the coal ignites by spontaneous combustion and burns

d A *teakettle* on a stove contains *water* that is boiling at a constant rate, the system boundary is fixed and crosses the spout

5. For each system of Prob 1 list, to the best of your knowledge, all the properties that could be used to identify the state. Are these intensive or extensive properties? Are they independent or dependent properties?

6. Are the systems of Prob 1 homogeneous or heterogeneous? Do phase changes occur?

7. Distinguish between atomic, chemical, internal, potential, and kinetic energy

8. Explain why heat and work are not properties of a system

9. An insulated torus is filled with water that is moving at a rate of  $100 \text{ ft sec}^{-1}$ . In a few seconds this velocity will be dissipated by friction and the system (of water alone) will assume an equilibrium state

a List the types of energy present before and after the dissipation process

b Does the energy of the system increase or decrease?

c Does the internal energy of the system increase or decrease?

10. Devise a number of systems wherein energy is transferred because of a temperature difference. Redefine the boundaries in the foregoing systems in order that the term *heat* can be used

11. Determine the conversion factors for the following: (a) joules to foot pounds, (b) kilowatts to horsepower

12. Calculate the potential energy in Btu of 1 lb<sub>m</sub> at an elevation of 100 ft above a datum of zero potential energy, if

$$(a) \ g = 30 \text{ ft sec}^{-2}$$

$$(b) \ g = g_0$$

13. Determine the kinetic energy and the final velocity that can be realized by transformation of the potential energy of Prob 12 without loss

14. Determine the maximum velocity that would be given to 1 lb<sub>m</sub> by proper transformation of 1000 Btu

15. a What is the minimum work that must be done per pound of water to pump 100 gal min<sup>-1</sup> of water, with density 62 lb<sub>m</sub> ft<sup>-3</sup>, to an open tank 100 ft above the pump? (Assume that the internal energy of the water remains constant and that  $g = g_0$ )

b If the water enters the tank with a velocity of discharge of 10 ft sec<sup>-1</sup>, how much work is required for the pumping operation?

c Determine the horsepower required by the pumping engine

16. a Calculate the enthalpy of 3 lb<sub>m</sub> of fluid that occupy a volume of 20 ft<sup>3</sup> if the internal energy is 1000 Btu lb<sub>m</sub><sup>-1</sup> and the pressure is 2 atm absolute

b If the pressure is 50 in Hg, what will be the value for enthalpy if other values remain unchanged?

### Symbols

<i>A</i>	area
Btu	British thermal unit
<i>C</i>	centigrade degree
cal	calorie
cgs	centimeter-gram-second (metric system)
<i>E</i>	energy in general
<i>e</i>	energy in general for unit mass of material (specific)
$\mathcal{E}$	electromotive force (emf) in volts
<i>F</i>	force
<i>F</i>	Fahrenheit degree
FE	flow energy
<i>g</i>	local acceleration of gravity
$g_c$	dimensional constant = $32.1739 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}$
$g_0$	standard acceleration of gravity
<i>g</i>	gram
<i>h</i>	enthalpy per unit mass (specific), $u + \frac{pv}{J}$ by definition (always in thermal units)
[ <i>H</i> ]	dimension of heat
hp	horsepower
<i>i</i>	electric current
<i>J</i>	Joule's equivalent
int	international units
IT	International Steam Table Conference units
kwhr	kilowatthour



<b>KE</b>	kinetic energy
<b>L</b>	length
<b>m</b>	mass, also, mass flow rate
<b>p</b>	pressure
<b>P</b>	power
<b>PE</b>	potential energy
<b>Q</b>	heat
<b>q</b>	electrical charge
<b>[T]</b>	dimension of temperature
<b>U</b>	internal energy (always in thermal units)
<b>u</b>	internal energy per unit mass (specific) (always in thermal units)
<b>V</b>	velocity, also, volume
<b>v</b>	specific volume
<b>w</b>	weight
<b>W</b>	work
<b>z</b>	height

**Greek Letters**

$\theta$	(theta)	time
$\delta$	(delta)	infinitesimal increment

**Subscripts**

<b>f</b>	force
<b>m</b>	mass

**CLASS ASSIGNMENTS**



## CHAPTER III

### THE FIRST LAW

Thermodynamics, heat power, and heat engineering are related terms comprising the laws or beliefs of man arising from the study of energy and its transformations during physical or chemical changes. Certain effects of energy, notably those accompanying a transfer of heat, have as a major result the production of work or power, and these effects are the primary interest of the engineer.

**3-1. The General Energy Equation.** The work of Joule and others led to the gradual acceptance of the premise called the *First Law of Thermodynamics*

**Energy can be neither created nor destroyed but only converted from one form to another.**

This statement of conservation of energy to be strictly correct must also carry the implication of conservation of mass although, in engineering calculations, energy balances can be made quite independently of mass balances

For any system the First Law states that the net result of heat or work will be a change in the energy of the system. The general energy equation is an expression of the First Law.

$$Q - W = E_2 - E_1 = \Delta E \quad (3-1)$$

where $Q$ = heat transferred	+ for heat added to the system
	- for heat subtracted from the system
$W$ = work done	+ for work done by the system
	- for work done on the system

$\Delta E$  = change in total energy of the system

Note that the change in energy of all types,  $\Delta E$ , in Eq (3-1) is entirely a system term and is measured by changes in properties of the system. Heat and work are energy effects external to the system (by definition) and are best measured by observation of changes in the surroundings. Equation (3-1) is simply an energy balance between system and surroundings and applies to any open or closed system. However, for the open system Eq (3-1) must be carefully treated, for mass as well as energy transfers will occur with the surroundings. The system may

have one or more flow streams entering and leaving, while energy and mass may accumulate within the system. An expanded form of Eq (3-1) can be written to separate the energy into that arising from mass flow into the system and that which will accumulate or be stored within the system

$$Q - W = \Delta E_{\text{flow}} + \Delta E_{\text{storage}} \quad (3-2)$$

and for more than one flow stream

$$Q - W = [\Sigma(m_{\text{out}}e_{\text{out}}) - \Sigma(m_{\text{in}}e_{\text{in}})]_{\text{flow}} + [m_2e_2 - m_1e_1]_{\text{storage}} \quad (3-3)$$

where subscript 2 = final state of the system

subscript 1 = initial state of the system

Flow energy cannot be stored in a system (Art 2-10), and when Eq (2-5) is substituted in Eq (3-3),

$$\begin{aligned} Q - W = & \sum \left[ m \left( u + \frac{pv}{J} + \frac{V^2}{2Jg_c} + \frac{g}{Jg_c} z \right) \right]_{\text{flow out}} \\ & - \sum \left[ m \left( u + \frac{pv}{J} + \frac{V^2}{2Jg_c} + \frac{g}{Jg_c} z \right) \right]_{\text{flow in}} \\ & + \left[ m_2 \left( u_2 + \frac{V_2^2}{2Jg_c} + \frac{g}{Jg_c} z_2 \right) - m_1 \left( u_1 + \frac{V_1^2}{2Jg_c} + \frac{g}{Jg_c} z_1 \right) \right]_{\text{storage}} \end{aligned} \quad (3-4)$$

Although Eq (3-4) appears quite formidable, it will be found that many of the terms are negligibly small or zero for practical systems. Such terms have been included here only for completeness of presentation.

For example, consider the storage term in Eq (3-4). In most cases kinetic energy, if present, will be quite small for the velocities that will be encountered in practical systems. Also, it is usually possible to measure<sup>1</sup> the change in storage energy by measurements made before flow (or the process) begins and after flow (or the process) stops. When this procedure is followed, the change in stored kinetic energy will be zero because a velocity cannot be maintained for any length of time in a closed and undisturbed system. A change in potential energy, while possible, will be of negligible value for the small size of equipment found in engineering. Thus, for most systems, Eq (3-4) can be reduced to

$$\begin{aligned} Q - W = & \sum \left[ m \left( u + \frac{pv}{J} + \frac{V^2}{2Jg_c} + \frac{g}{Jg_c} z \right) \right]_{\text{flow out}} \\ & - \sum \left[ m \left( u + \frac{pv}{J} + \frac{V^2}{2Jg_c} + \frac{g}{Jg_c} z \right) \right]_{\text{flow in}} + [m_2u_2 - m_1u_1]_{\text{storage}} \end{aligned} \quad (3-5)$$

<sup>1</sup> See Art 9-19

In the flow terms of Eq (3-5), proper selection of conduit sizes allows the kinetic-energy terms to cancel or results in low velocities that can be neglected. Unless radical differences in elevation are present, potential-energy terms will approach zero magnitude. With these simplifications and the introduction of the convenient property of enthalpy (Art 2-11) into Eq (3-5),

$$Q - W = \Sigma[mh]_{\text{flow out}} - \Sigma[mh]_{\text{flow in}} + [m_2 u_2 - m_1 u_1]_{\text{storage}} \quad (3-6)$$

The use of these equations will be illustrated in this and following chapters

**3-2. The Closed System.** Either Eq (3-1) or (3-4) can be directly applied to a closed system noting only that the change in total energy is for a nonflow system that contains a constant mass of material. In this case Eq (3-4) can be reduced [or Eq (3-1) can be expanded] to the form

$$Q - W = m \left( \Delta u + \Delta \frac{V^2}{2Jg_c} + \Delta z \frac{g}{Jg_c} \right)_{\text{storage}} \quad (3-7a)$$

In the absence of potential-kinetic effects this equation can be written

$$Q - W = \Delta U \quad (3-7b)$$

and for unit mass of the system,

$$Q - W = \Delta u \quad (3-7c)$$

In using these equations for analysis, the structural parts of the system can be considered to approach zero mass, hence, they need not affect the process undergone by the fluid. However, for real processes performed in the laboratory, the change in internal energy of all the mass or masses in the system must be included.

*a Constant-volume Process* In Fig 3-1a the *constant-volume* system is receiving heat of amount  $Q$ . The restriction of constant volume prevents energy from entering (or leaving) the system as compression (or expansion) work because the boundary is fixed and immovable. When Eq (3-7b) is applied,

$$Q - W = \Delta U$$

Assuming that neither electrical nor other mechanical work transfers occur,

$$\begin{aligned} Q - 0 &= \Delta U \\ Q &= \Delta U = U_2 - U_1 \end{aligned} \quad (3-8)$$

Equation (3-8) is quite valid if the restriction that work effects are zero is remembered. However, it is not permissible to examine the change in internal energy of a constant-volume system and then declare that this change is equal to the heat added. For consider Fig 3-1b. Here mechanical work is introduced into the system from the surroundings and by paddling the fluid and so dissipating the work the same change

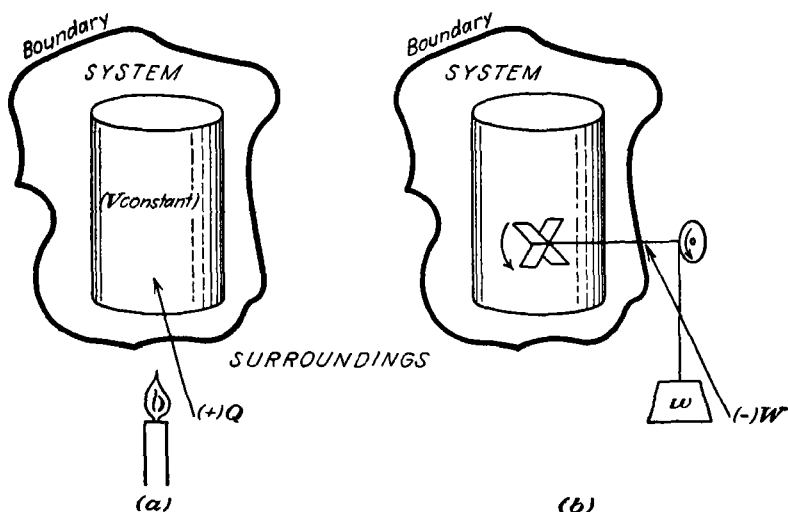


FIG 3-1 Constant volume process, nonflow system (The boundary is an imaginary surface that separates system and surroundings)

in internal energy can be produced as was evident from a transfer of heat. By Eq (3-7b)

$$Q - W = \Delta U$$

Since  $Q = 0$ ,

$$-W = \Delta U = U_2 - U_1 \quad (3-9)$$

(By definition work done *on* a system is negative; hence,  $\Delta U$  will be positive in sense.)

This example emphasizes that heat and work are *by definition* boundary effects and must be identified at the boundary because the effect of heat and work can be the same. The properties of the system cannot be used to identify either heat or work. In other words, the process or path that the system experiences is not sufficient evidence by itself to be used for recognizing or measuring either heat or work.

The system of Eq (3-9) can be cooled to the original state by abstracting an amount of heat given by Eq (3-8), and these two processes can be operated over and over again. The net effect of the

combination of processes is

$$\begin{aligned} Q - W &= 0 \\ Q &= W \end{aligned} \quad (3-10)$$

*In this manner work can be completely and continuously converted into heat*

*b Friction* The result of a paddling operation such as described above will be evidenced by a rise in temperature of the fluid (or by a phase change without change in temperature) To obtain the same thermal effect, heat could have been transferred instead of work The process as performed is a *frictional* process

**Friction is the term used when a change occurs through the transfer of work that could have been attained in whole or in part by a transfer of heat.**

Thus, the term *friction* implies a thermal (heating) effect Any operation that expends work by inducing a chaotic turbulence in a viscous fluid is a frictional process

*Mechanical friction* may be present in the system If two masses are rubbed together, the abrasion of the surfaces causes a rise in temperature of the rubbing parts Internal energy will transfer from the region of high temperature to the region of lower temperature Work is dissipated with the same end result as would be experienced by transfer of heat The letter *F* will be used to designate the energy expended in any form of friction

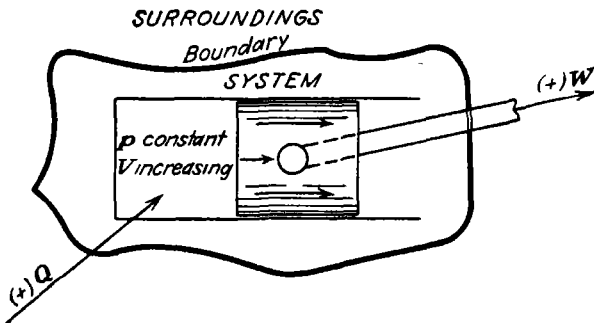


FIG 3-2 Constant pressure expansion process, nonflow system

*c Constant-pressure Process* In Fig 3-2 the system will be defined to include both working fluid *and* the piston and cylinder This system is receiving heat *Q*, carefully regulated to ensure that the fluid is always at the same pressure The expansion of the fluid will move the



piston that is connected to an external load. This is a *constant-pressure* process of a closed system with movable boundaries. Applying Eq (3-7b),

$$Q - W = \Delta U$$

$$Q = \Delta U + W$$

and

$$-W = \Delta U - Q$$

These equations do not attempt to predict the amount of heat that must be added or the maximum amount of work that can be realized from the constant-pressure process. The First Law can only show an energy balance that must exist between system and surroundings. For any fixed increase of internal energy,  $Q$  and  $W$  may be varied from the extreme of zero heat to zero work transfer. Heat transfer can be made zero by paddling the fluid to increase the internal energy, as was done for the constant-volume system. Work can be made zero by the presence of mechanical friction between piston and cylinder within the system (by definition of the boundary). Heat can be added and the pressure can be held constant, but for this system of fluid and mechanical parts no useful work need be done on the surroundings.

*d Adiabatic Process* An *adiabatic process* is a change of state accomplished without transfer of heat. In Fig 3-3 the system con-

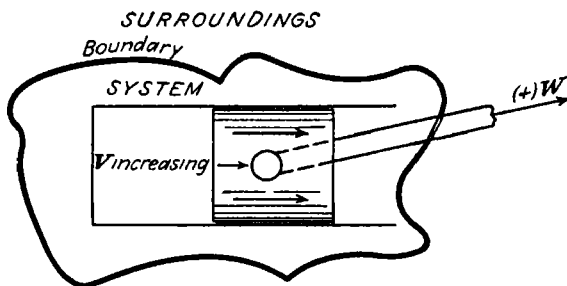


FIG 3-3 Adiabatic expansion process, nonflow system

sists of fluid, piston, and cylinder. The fluid is expanding and is thereby moving the piston. Work may be done. To repeat Eq (3-7b),

$$Q - W = \Delta U$$

The condition of an adiabatic process that no heat is to be transferred can be approached if the process is quickly performed, and for the limiting condition of  $Q = 0$ ,

$$W = -\Delta U = U_1 - U_2$$

Again, no assumption need be made as to the perfection of the process. The work output from the adiabatic expansion may be zero or greater than zero. Indeed, the presence of friction could entirely prevent the piston from moving.

*e. Isothermal Process* In Fig 3-4 the system of fluid and mechanical parts is maintained at a constant temperature by transfer of heat while expansion (or compression) proceeds. This is an *isothermal* or *constant-temperature process*.

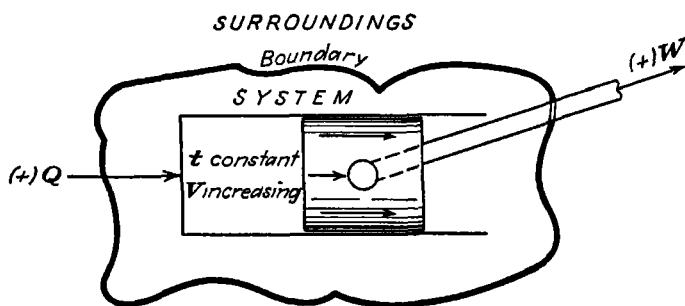


FIG 3-4 Isothermal expansion process, nonflow system

*f Constant-internal-energy Process* In the previous case, heat could have been transferred at a rate such that the internal energy of the system would have been held constant. By Eq (3-7b),

$$\begin{aligned} Q - W &= \Delta U = 0 \\ Q &= W \end{aligned} \quad (3-11)$$

The work output from the *constant-internal-energy* expansion can be zero or greater than zero. The First Law merely requires that transfers of heat and work be equal if the internal energy of the system is to remain constant.

A series of two processes has already been devised to convert continuously work into heat [Eq (3-10)]. Equation (3-11) specifies a process for producing an amount of work exactly equal to the quantity of heat added. However, this process cannot be continuously operated because at some stage of the expansion the piston will have to be restored to the initial position, and this will require transfers of both heat and work.

A famous experiment, first performed by Joule and now called a *Joule expansion*, is illustrated in Fig 3-5. Container A, filled with air at a medium pressure, is connected by a valve to container B, which is evacuated. Both containers are immersed in water at room

temperature When the valve is opened, the air in container *A* expands and pushes part of the contents into container *B*. The air

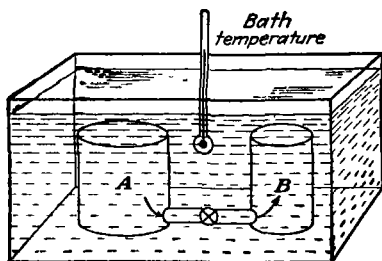


FIG 3-5 Joule's free expansion experiment

doing this operation undergoes a quick expansion, and its temperature decreases. Meanwhile, the air first entering *B* is being compressed by the incoming flow, causing its temperature to increase. But, after equilibrium has been restored, it will be found that the change in temperature for the entire process (as shown by the bath thermometer) will approach zero. Joule thought the temperature change was zero

and concluded from this experiment, for the system of air alone,

$$Q - W = \Delta U$$

and

$$Q, W = 0$$

Therefore,

$$\Delta U = 0$$

and

$$U_1 = U_2$$

That is, the internal energy of air must be a function only of temperature; for pressure and specific volume changed, but temperature and internal energy were constant. More precise tests on air and other fluids show that a small drop in temperature is always evident.

**For gases at low pressures it can be assumed that the internal energy is related only to temperature and therefore is not affected by changes in pressure (Joule's law).**

Such a procedure allows simple (but approximate) solutions to be found for many complicated problems where the exact solutions are quite difficult to obtain.

An adiabatic expansion of this type without the performance of work is called a *free expansion* or, better, a *Joule expansion* ( $\Delta U = 0$ ).

**3-3. The Open System.** An open system has transfers of mass as well as of energy with the surroundings, and Eq (3-4) is the general equation. Here the evaluation of the storage term presents some difficulties; but, if the system can be made to pass periodically through the same state, then, for measurements of  $Q$ ,  $W$ , and  $\Delta E_{\text{flow}}$  beginning

and ending with the attainment of this state, the storage term will be zero. For most engineering systems either the storage term is zero or the periodic fluctuations in value are of a smaller order than the accuracy of the experiment. For these cases Eq. (3-4) reduces to

$$Q - W = \Delta E_{\text{flow}} \quad (3-12)$$

Under Eq. (3-12) comes a most important group of devices that are called steady-flow systems

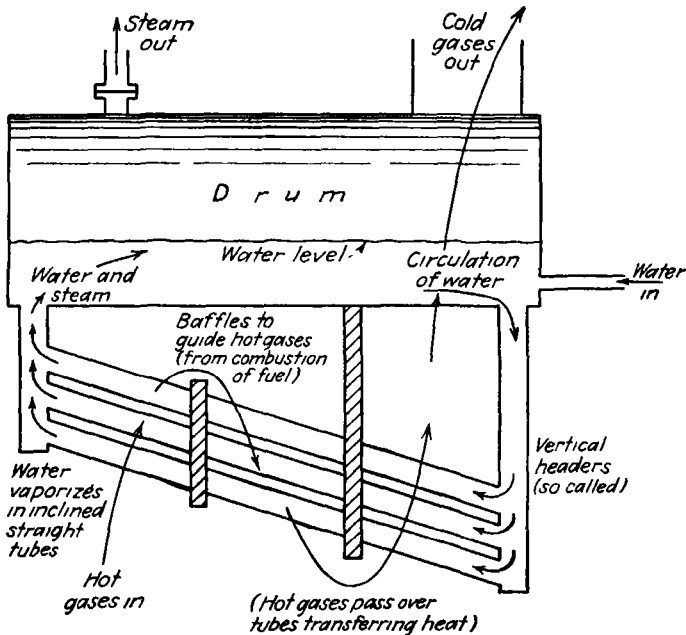


FIG 3-6 Water tube boiler

**A steady-flow open system is one wherein all conditions and events at the boundary are unaffected by time.**

To fulfill this definition the following conditions must be satisfied

1.  $\Delta E_{\text{storage}}$  must be zero
2. The mass flow into the system must equal the mass flow out of the system. If this were not so, the system must continually increase or decrease in size with time.
3. The properties of the fluid entering and the properties of the fluid leaving the system must be constant (but, usually, not equal) in value.
4. Heat and work transfers must proceed at a constant rate

An example of a steady-flow open system is a boiler (Fig 3-6) Water enters the boiler at a constant mass rate while steam leaves the system at an equal mass rate. Heat must be transferred of amount equal to  $\Delta E_{\text{flow}}$ . When the boiler is first started, the system contains cold water and also the cold boiler shell, and several hours of firing must elapse before a *steady state* has been reached. During this period of time the heat supplied must equal  $\Delta E_{\text{flow}} + \Delta E_{\text{storage}}$ .

The term *steady flow* implies that a steady state has been attained if all mass and energy transfers at the boundary are to be invariant with time.

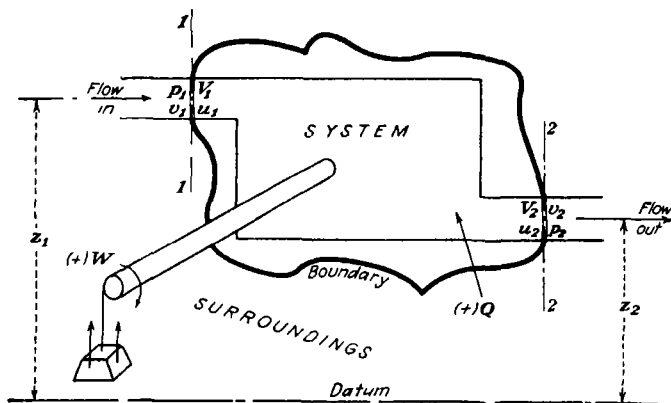


FIG 3-7 Steady-flow system of one flow path (The boundary is an imaginary surface that separates system from surroundings)

**3-4. The Steady-flow Energy Equation.** The simplest example of steady flow is a system with only one flow circuit as illustrated in Fig 3-7. For this system Eq (3-4) reduces to

$$Q - W = m(u_2 - u_1) + \frac{m(p_2 v_2 - p_1 v_1)}{J} + \frac{m(V_2^2 - V_1^2)}{2Jg_c} + \frac{mg}{Jg_c} (z_2 - z_1) \quad (3-13a)$$

$$Q - W = m(h_2 - h_1) + \frac{m(V_2^2 - V_1^2)}{2Jg_c} + \frac{mg}{Jg_c} (z_2 - z_1) \quad (3-13b)$$

where $Q$ = heat transferred	+ if added to system
	- if abstracted from system
$W$ = work transferred	+ if done by system
	- if done on system

Equation (3-13) is called the *general energy equation for steady flow* (although, in truth, Eq (3-4) is more general).

Throughout this text, work, and not power, will be most often calculated; thus the mass flow  $m$  in Eq (3-13) is considered to have the dimension of mass. When  $m$  is considered to be a mass flow rate, then  $Q$  and  $W$  will also be rates and the symbol for work,  $W$ , should be replaced by the symbol for power,  $P$ .

$$P = (W \text{ Btu/lb}_m)(m \text{ lb}_m/\text{sec}) = \text{Btu/sec}$$

No symbol is assigned to the heat rate because it is rarely used, in fact, the term has another meaning than implied here (Art 12-8).

**Example 1:** A system has a flow rate of  $5 \text{ lb}_m \text{ sec}^{-1}$ . The enthalpy, velocity, and height at the entrance are, respectively,  $1000 \text{ Btu lb}_m^{-1}$ ,  $100 \text{ ft sec}^{-1}$ , and  $100 \text{ ft}$ . At the exit these quantities are  $1020 \text{ Btu lb}_m^{-1}$ ,  $50 \text{ ft sec}^{-1}$ , and  $0 \text{ ft}$ . Heat is transferred to the system at the rate of  $50 \text{ Btu sec}^{-1}$ . How much work can be done by this system?

**Solution:** When Eq (3-13b) is used for unit mass,

$$\begin{aligned} Q - W &= (h_2 - h_1) + \left( \frac{V_2^2 - V_1^2}{2Jg_c} \right) + \frac{g}{g_c} \left( \frac{z_2 - z_1}{J} \right) \\ \frac{50}{5} - W &= (1020 - 1000) + \left( \frac{50^2 - 100^2}{2(32.2)(778)} \right) + \frac{32.2}{32.2} \left( \frac{0 - 100}{778} \right) \\ 10 - W &= 20 - 0.15 - 0.13 \\ W &= -9.7 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

This answer, when multiplied by the mass flow rate ( $\text{lb}_m/\text{sec}$ ) has the dimension of power

$$P = -48.5 \text{ Btu/sec} \quad \text{Ans}$$

Note that work (or power) must be supplied to the system, a condition indicated by the negative sign of  $W$ .

**3-5. The Continuity Equation.** As unit mass of fluid enters the open system, a condition for steady flow demands that, in the same period of time, unit mass of fluid must leave the system

$$m_1 = m_2$$

and

$$m_1 \frac{\text{lb}_m}{\text{sec}} = \frac{A_1 (\text{ft}^2) V_1 \left( \frac{\text{ft}}{\text{sec}} \right)}{v_1 \left( \frac{\text{ft}^3}{\text{lb}_m} \right)} = m_2 = \frac{A_2 V_2}{v_2} \quad (3-14)$$

Equation (3-14) is called the *continuity equation of steady flow*.

The velocity  $V$  at any section of the system can be calculated from Eq (3-14), and it represents the *average* velocity at that section. It is customary to use this average velocity in the expression for kinetic

energy although the resulting value is somewhat in error<sup>1</sup>. Note that for the normal flow of fluid in a pipe the velocity at the wall will be zero, while near or at the center of the pipe velocity will be a maximum. Since each element of mass has kinetic energy in proportion to its velocity squared, then the kinetic energy of the entire mass is proportional to the average of the sum of the *squares* of the individual velocities. Since kinetic energy values may be relatively small, the difference in kinetic-energy values computed by using the average velocity is usually insignificant.

**Example 2:** For the data of Example 1 what must be the diameter of the round inlet pipe if the specific volume of the fluid is  $15 \text{ ft}^3 \text{ lb}_m^{-1}$ ?

**Solution:** From Eq. (3-14)

$$m = \frac{AV}{v}$$

$$5 = \frac{A(100)}{15}$$

$$A = 0.75 \text{ ft}^2 = 108 \text{ in}^2$$

$$D = 11.7 \text{ in}$$

### 3-6. Applications of the Steady-flow Energy Equation. (a) Boiler

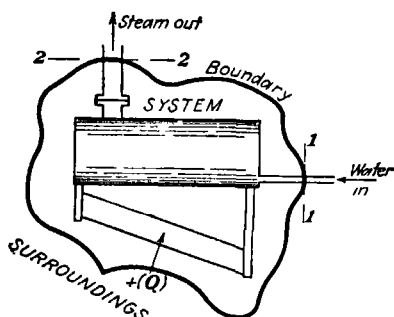


Fig. 3-8 System of boiler and single flow path of water-steam (Flow path of hot gases is in the surroundings)

A steady-flow system that has already been mentioned is the boiler, and the thermodynamic elements of this system are illustrated by Fig. 3-8. Here no work is done by or on the system while the difference in height between the inlet and the outlet flow is of negligible consequence. The velocities of flow are held at low values by selection of proper pipe size. Then,

$$W = 0 \quad \Delta z \approx 0 \quad \Delta \frac{V^2}{2g_c} \approx 0$$

For this system, Eq. (3-13) can be written

$$Q = h_2 - h_1 \text{ Btu/lb}_m \quad (3-15)$$

Note that the heat added in the constant-volume process was  $\Delta u$ ; in this steady-flow process the heat added is  $\Delta h$ .

**b. Reciprocating-piston Pump** The usual machine for compressing gases consists of a cylinder with *double-acting piston*, that is, compres-

<sup>1</sup> Note Art. 9-8, and Example 7

sion occurs on both sides of the piston. In Fig. 3-9, movement of the piston allows gas to be drawn into the cylinder at *A* while gas trapped on the other side of the piston *B* is being compressed. The compression of the gas is regulated by the receiver pressure because the outlet (and inlet) valves are merely check valves. Figure 3-10a illustrates a

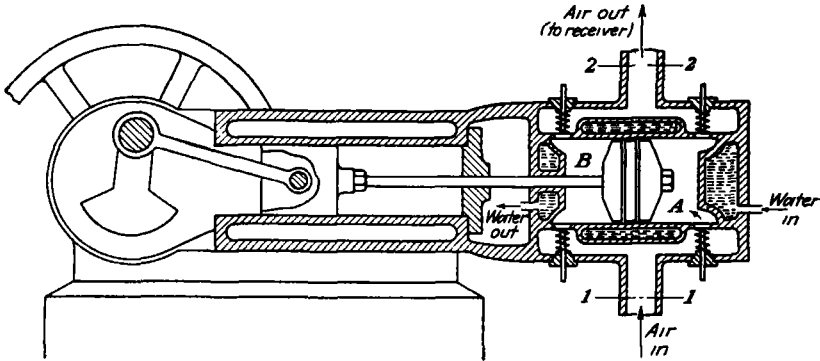


FIG 3-9 Reciprocating-piston double-acting air compressor

spring check valve. During the compression stroke the flat spring flaps are held against the discharge ports of the compressor by the pressure in the receiver. When the gas being compressed reaches a pressure higher than that in the receiver, the flaps are forced away from the ports and gas is discharged into the receiver. When the

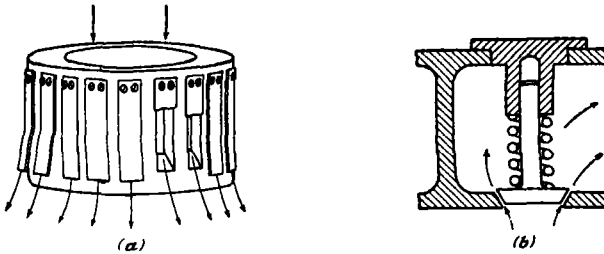


FIG 3-10 Check valves for air compressors (a) Feather valve for inlet or discharge ports, also made as a disk with spring flaps (b) Poppet valve for discharge port

piston reaches the end of the compression stroke and starts the return stroke, the pressure in the cylinder falls, causing the receiver pressure to close the discharge valve. The piston cannot deliver all the air in the cylinder to the receiver because a *clearance* must be allowed to prevent the piston from striking the cylinder head at the end of the stroke. As the piston moves downward on the intake stroke, the pressure in the cylinder will not reach atmospheric (or the suction



pressure) until the high-pressure gas in the clearance space has been expanded. After this point has been reached, the inlet valve (Fig 3-10) will open because the atmospheric pressure is higher than the pressure in the cylinder. The remainder of the stroke is the true

intake stroke. This *reciprocating-piston* compressor is an example of a *positive-displacement* machine.

Most, if not all, pistons have *piston rings* (Fig 3-11) to prevent leakage of the gas during compression. The ring is a cast-iron circular segment that is slipped over the piston and into the piston-ring groove. When the piston is inserted in the cylinder, the ring is constrained to its original circular shape and thus will exert a pressure against the cylinder wall. The mechanical friction of piston rings and piston rubbing against the cylinder causes the temperatures of these parts to rise. Since the fluid being compressed also experi-

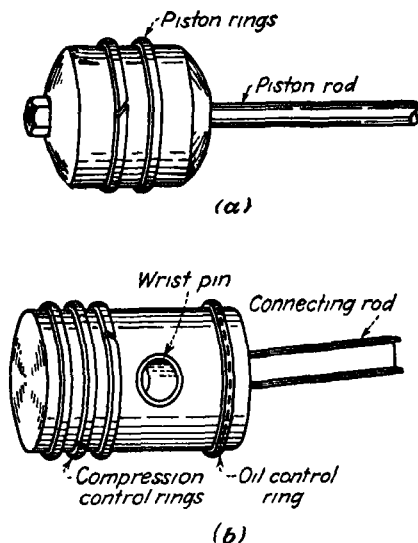


FIG 3-11 Pistons and piston rings (a) Double-acting air-compressor piston (b) Single-acting combustion-engine piston

ences a rise in temperature, cooling of the cylinder is necessary to prevent seizing or scoring of the close-fitted parts.

Although the flow in and out of the cylinder is intermittent, by selecting the inlet and outlet boundaries of the system at some distance from the cylinder the flow may be considered essentially steady. Applying Eq (3-13) to the diagrammatic system of Fig 3-12,

$$Q - W = h_2 - h_1 \quad \text{when } V_1 \approx V_2$$

or

$$W = h_1 - h_2 + Q$$

No assumption is made as to the perfection either of the mechanism or of the process. Here the imperfections of the mechanism will cause not only an increase in the internal energy of the working fluid from undesirable turbulence but also an increased heat transfer from friction of the piston and piston rings on the cylinder. Note that the work

computed by the above formulas is not an ideal value but an actual value for a real machine

In practice,  $Q$  would be difficult to determine for the entire system because it would include not only heat transferred to the cooling

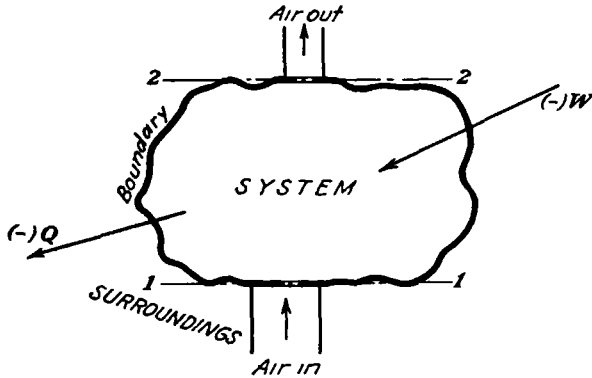


FIG 3-12 System of air compressor and single flow path of air. (Flow path of cooling water is in the surroundings)

water but also heat transferred by radiation and conduction to the surroundings.

In compressing fluids it is well to remember that the work required is measured both by the force applied and the distance of application

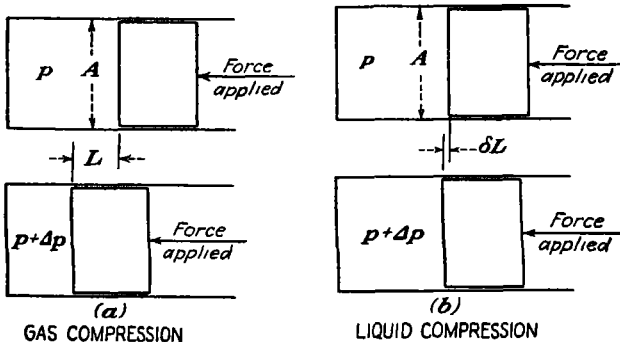


FIG 3-13 Comparison of gas and liquid compression processes

of the force In Fig 3-13a a gas is compressed from  $p$  to  $p + \Delta p$ , while the piston is moving a distance  $L$ . If  $\Delta p$  is small, the work is approximately equal to

$$W \approx pAL$$

If a liquid is substituted for a gas, the piston can move only the infinitesimal distance  $\delta L$  before the pressure has increased from  $p$  to

$p + \Delta p$ , and the work is approximately

$$W \approx pA\delta L$$

Obviously, the work necessary to compress a liquid is only a small fraction of that necessary to compress a gas through the same pressure range because  $\delta L$  is but a small fraction of  $L$  (Of course, the internal energy of the gas is proportionately increased by compression while that of the liquid is little affected) However, the total work required for a steady-flow liquid pump may be considerable even though compression work is negligible because work is also necessary to produce the flow energy of the liquid

*c. Centrifugal Pump* Centrifugal pumps similar to those shown in Fig 3-14a, b, and c are used to pump gases or liquids The fluid enters the inlet at 1 and passes into the *impeller* where part of the compression occurs as a result of the radial flow of the fluid induced by centrifugal force The fluid leaving the impeller has a high velocity, and, when this velocity is reduced by the *diffuser* or by a *scroll case*, the pressure is again increased Thus, compression occurs without positive displacement of the fluid In this and in most open systems, the change in potential energy is insignificant in comparison with the change in other properties, the change in kinetic energy approaches zero if, as is the usual case, the entering and leaving pipes are proportioned to give reasonably low (or equal) values for the average velocity Applying Eq (3-13) with the above thoughts in mind,

$$Q - W = h_2 - h_1 \text{ Btu/lb}_m$$

Since no means are indicated for cooling the machine, heat transferred to or from the real system will result from unavoidable radiation or convection If the temperature of the fluid is of the same order as that of the surroundings, or if a high rate of flow is maintained, the heat loss per unit of mass of fluid will be slight and can be considered to be zero Hence,

$$\begin{aligned} W &= J(h_1 - h_2) \text{ ft lb}_f/\text{lb}_m \\ P &= mJ(h_1 - h_2) \text{ ft lb}_f/\text{sec} \\ m &= \text{mass flow rate lb}_m/\text{sec} \\ h &= \text{enthalpy Btu/lb}_m \\ J &= 778 \text{ 16 ft lb}_f/\text{Btu} \end{aligned}$$

The horsepower required to drive the pump equals

$$\text{hp} = \frac{mJ(h_1 - h_2)}{550} = \frac{m(h_1 - h_2)}{0.706}$$

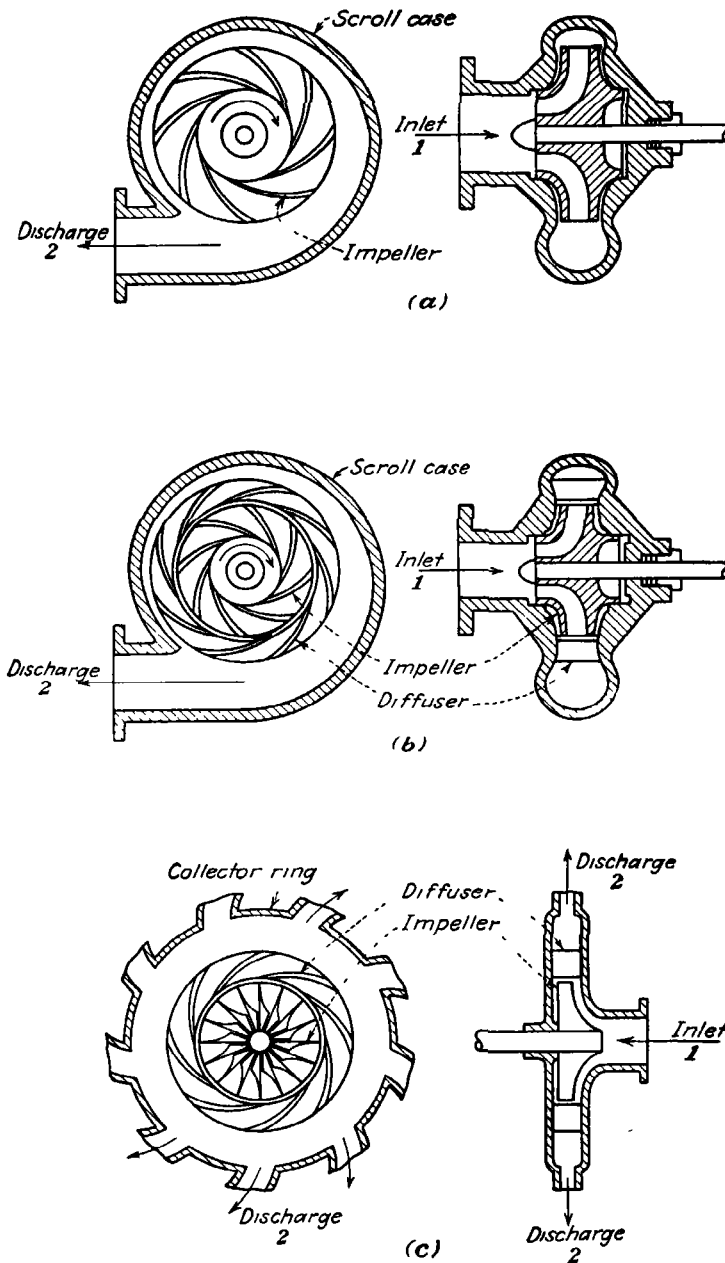


FIG 3-14 Pumps, fans, blowers, and compressors (a) Volute liquid pump (b) Diffuser or turbine liquid pump (c) Centrifugal supercharger

The above computations indicate that all the energy transferred to the system as work could be accounted for by changes in the properties of the working fluid. This does not imply that the mechanism of the system and the process is ideal. For instance, work will be necessary to overcome friction in the bearings, and the effect of this friction will be to raise the temperature of the structural parts. The analysis implies that, since  $Q$  can be considered zero, the parts are continuously cooled and kept at a constant temperature by the working fluid. The work put into the machine to overcome friction reappears as an increase in internal energy of the working fluid. In a similar manner, part of the work put into the system may be dissipated in creating undesirable turbulence of the fluid, and this energy also reappears as an increase in internal energy of the fluid. The analysis makes no attempt to set up an ideal process and is simply an energy balance for the real (or ideal) system under observation.

Flow through the centrifugal pump is continuous and at a high velocity, while in the reciprocating pump the flow is intermittent and at low velocities. For these reasons the size of the centrifugal pump is only a fraction of the size of a reciprocating machine that is able to handle the same mass flow. But accompanying this advantage is the disadvantage that high velocities cause undesirable turbulence and therefore a greater work input. Since, relative to liquids, a large amount of work is required to compress a gas, any increased work necessary because of the inefficiency of the machine will cause a proportionate increase in cost that is already high. For this reason centrifugal pumps are used to compress gases only through limited pressure ranges. In pumping liquids, although the same inefficiencies exist, the smaller amount of work required to compress a liquid makes the loss from turbulence less serious, especially when the initial cost and size of the pump are considered. The centrifugal pump is universally used for pumping liquids unless the mass flow rate is minute.

Compressors of any type can be analyzed in the same manner as the centrifugal pump. A *fan* (Fig. 3-14*d* and *e*) is used to displace large quantities of air or gas with little pressure rise (for purposes such as ventilation), while a *blower* (Fig. 3-14*c* and *f*) is used to force air under pressure. In the Roots blower the air is trapped between the casing and the lobes of the rotor, and compression of the air does not begin until the outlet has been uncovered. The Roots blower, unlike other rotary compressors such as the centrifugal supercharger, is a *positive displacement* compressor because a definite quantity of fluid is displaced in each revolution of the rotor. An *axial-flow* compressor is

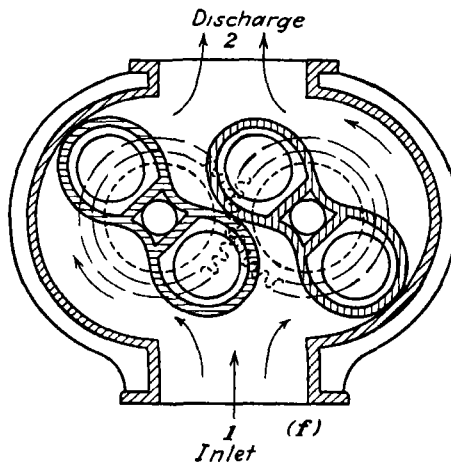
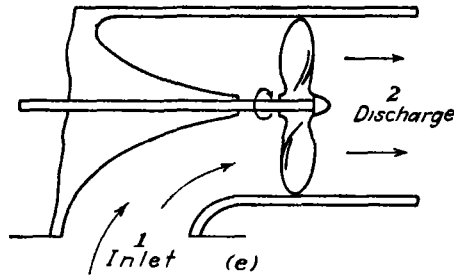
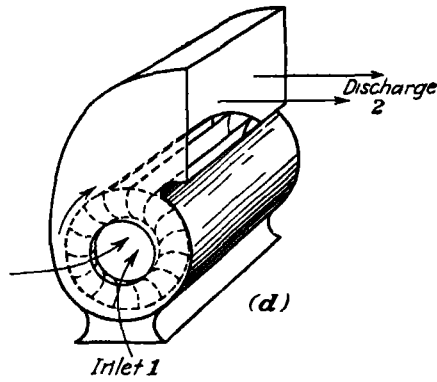


FIG 3-14 (*continued*) Pumps, fans, blowers, and compressors (d) Centrifugal fan (low pressure 1-20 in  $H_2O$ ) (e) Tubeaxial fan (low-pressure propeller wheel) (f) Roots blower (medium pressure 15-30 psi).

shown in Fig. 3-14g. Here are numerous *stages* of airfoil section blades so arranged that the fluid is accelerated by the moving blades

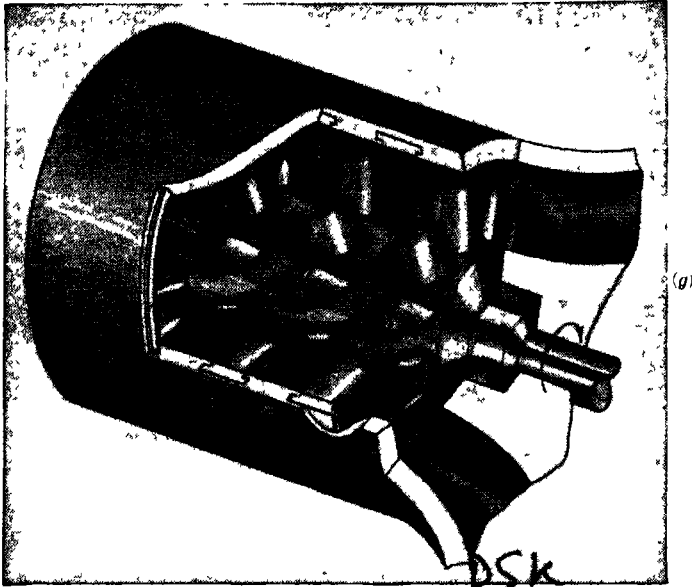


FIG 3-14 (continued) Pumps, fans, blowers, and compressors (g) Axial flow compressor

The fluid is then slowed down, and kinetic energy is transformed into pressure energy. By using a large number of stages, the kinetic increase in each stage is small and the efficiency of transformation is high.

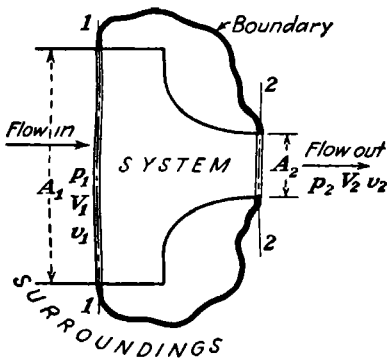


FIG 3-15 Nozzle

*d Nozzle.* A nozzle (Fig 3-15) is a device used to transform internal energy into kinetic energy. Fluid enters the nozzle at high pressure and expands to a lower pressure maintained by some means at the exit. For the system shown in Fig 3-15, little heat is transferred (by radiation, etc.), and no work is done. Applying Eq. (3-13),

$$Q - W = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2Jg_c} = 0$$

or

$$\frac{V_2^2 - V_1^2}{2Jg_c} = h_1 - h_2 \quad (a)$$

A relationship between  $V_1$  and  $V_2$  can be found from the continuity equation.

$$\frac{A_1 V_1}{v_1} = \frac{A_2 V_2}{v_2}$$

or

$$V_1^2 = V_2^2 \left( \frac{A_2 v_1}{A_1 v_2} \right)^2$$

Substitution of this value in Eq (a) gives

$$\frac{V_2^2}{2Jg_c} \left[ 1 - \left( \frac{A_2 v_1}{A_1 v_2} \right)^2 \right] = h_1 - h_2$$

$$V_2 = F_c \sqrt{2Jg_c(h_1 - h_2)} \quad (3-16)$$

where  $F_c$  is called the *correction factor* for initial velocity and equals

$$F_c = \left[ \frac{1}{1 - \left( \frac{A_2 v_1}{A_1 v_2} \right)^2} \right]^{\frac{1}{2}} \quad (3-17)$$

When the initial velocity is small, the correction factor approaches a value of unity and can be neglected

Do these formulas predict the maximum velocity that will be attained? No, because a porous plug at the exit of the nozzle would cause a profound change in the velocity. Similarly, a nozzle with rough walls would cause a like decrease. These formulas merely indicate the relationship between properties that must be maintained in any nozzle, real or ideal

*e. Throttling Process* Whenever fluid expands from a region of relatively high pressure to a region at a lower pressure, either work can be done or changes in kinetic or potential energy can be produced. In the absence of these energy transformations the process is literally described by the name *throttling*. In Fig 3-16 a valve is used to throttle the flow, although any other restrictive device could have been substituted. The fluid expanding through the valve

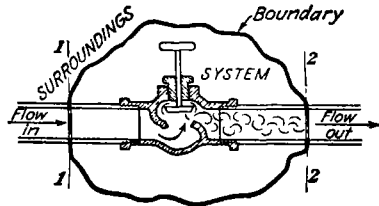


FIG 3-16 Throttling through globe valve

acquires a high velocity, which is dissipated in aimless turbulence of



the fluid When it is considered that either the expansion or the kinetic energy produced by the expansion could have been utilized to do work, it is evident that throttling is an undesirable process

Applying Eq (3-13) to the throttling process of Fig 3-16,

$$Q - W = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2Jg_c} \quad (Q \text{ and } W = 0)$$

The change in velocity in most systems will be small, or it can be made zero by proper selection of pipe sizes For this condition

$$h_1 = h_2 \quad (3-18)$$

This steady-flow throttling process has become known as the *Joule-Thomson expansion* ( $\Delta h = 0$ ) It is usual to consider that heat trans-

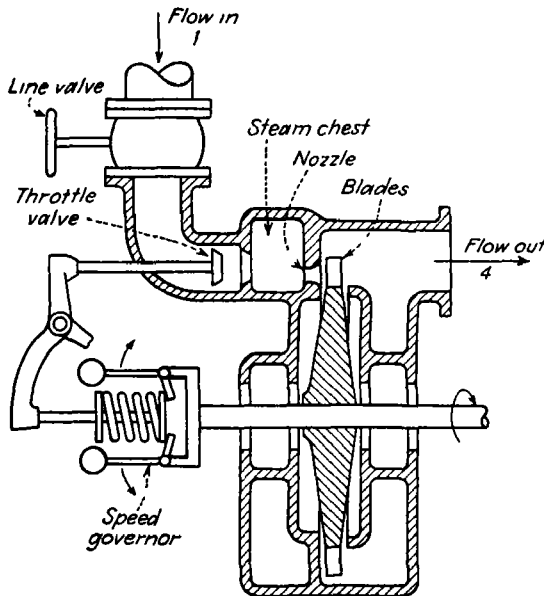


FIG 3-17 Elements of steam or gas impulse turbine

fer is zero because throttling in general occurs at a section that has little length

*Throttling and friction* affect the properties of the fluid to the same degree as a transfer of heat *Friction dissipates work while throttling dissipates energy that could have been transformed into work* The result of either factor is a thermal change that could have been accomplished by transfer of heat, and for this reason the term *friction* will be used as a general synonym for such losses The symbol of designation

for energy spent in throttling will be the same as that for friction, namely,  $F$ .

*f Gas or Steam Turbine* The elements of a small steam turbine (Fig 3-17) are essentially similar to those of a gas turbine, and the same explanation will apply to either machine. Steam at high pressure passes through a regulating or *throttle*<sup>1</sup> valve and enters the *steam chest*. Upon leaving the steam chest, the steam enters one or more nozzles that are located adjacent to a wheel or rotor. Along the periphery of this wheel are the *blades* or *buckets*. The steam passing through the nozzle expands and attains a high velocity with correspondingly high kinetic energy. The high-velocity stream leaves the nozzle and impinges on the blading, causing it to move. (Accordingly, a turbine of this type is called an *impulse turbine*.) As each blade rotates out of the path of the high velocity steam jet, another blade takes its place, and a continuous rotational force is thus applied to the wheel (Fig 3-18). The speed of the wheel is controlled by the *governor* (Fig 3-17). If the load is decreased and the turbine overspeeds, centrifugal force will cause the governor weights to move outward and tend to close the throttle valve. As the throttle is closed, the pressure in the steam chest decreases, the drop in pressure through the nozzle also decreases, and lower velocity is attained by the steam and therefore less impulse is given to the turbine wheel.

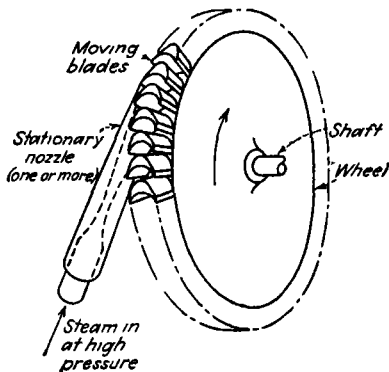


FIG 3-18 Nozzle and blading of impulse turbine

It may be of interest to examine the mechanism whereby work can be done by a jet of high-velocity fluid. In Fig 3-18 the fluid leaves the nozzle at high velocity and enters the curved-blade passage. A diagrammatic sketch of the vector velocities and blade shape appears in Fig 3-19. The initial absolute velocity  $V_1$  has a velocity relative to the blade of  $V_r$  because of the blade speed  $V_b$ . The contour of the blade causes the direction of the fluid to be reversed, thus exerting a force on the blade. The fluid leaves the blade without change in value of the relative velocity if friction is absent. The absolute velocity of the fluid leaving the blade is the sum of  $V_r$  and  $V_b$  as shown. The work done can be found by calculating the force exerted on the blade or more simply by finding the decrease

<sup>1</sup> The line valve is also frequently called the throttle even though this valve is not used to throttle the steam (except, of course, in starting), similarly, line pressure is unfortunately called the pressure at the throttle.

in energy of the fluid. In the absence of friction the fluid will not be changed by this process, and the work done will equal the change in kinetic energy for the fluid. From Fig 3-20 and the flow equation (3-13),

$$Q - W_{\text{blade}} = h_3 - h_2 + \frac{V_3^2 - V_2^2}{2Jg_c}$$

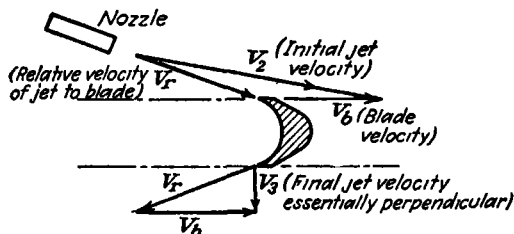


FIG 3-19 Ideal velocities in nozzle and blade (no friction)

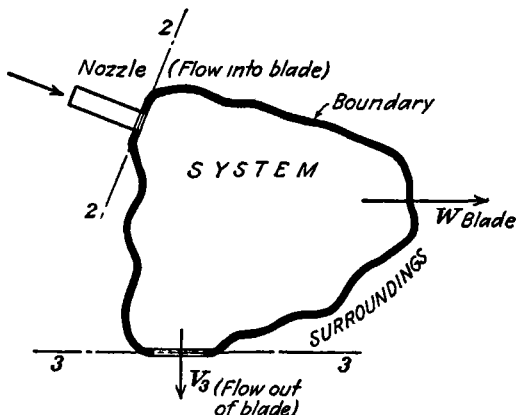


FIG 3-20 Adiabatic system for flow through turbine blade (Nozzle is in the surroundings)

But  $Q = 0$  and  $\Delta h = 0$  (no friction), therefore,

$$W_{\text{blade}} = \frac{V_2^2 - V_3^2}{2Jg_c}$$

If friction is present,  $\Delta h$  is not zero and

$$W_{\text{blade}} = h_2 - h_{3'} + \frac{V_2^2 - V_{3'}^2}{2Jg_c}$$

The effect of friction is a decrease in velocity of the fluid, and this dissipation of kinetic energy causes the enthalpy to increase with less work done by the system. A relationship can be found for the enthalpy and velocity changes across a blade for conditions of friction, for if friction is present, the velocity relative to the blade will decrease as flow proceeds across the blade. Consequently, the relative

velocity entering the blade will be larger than the relative velocity leaving the blade, while the dissipation of kinetic energy will be reflected in an increase in enthalpy of the fluid. To an observer standing on the blade, the blade will be stationary while the fluid enters with velocity  $V_r$  and leaves with velocity  $V_{r'}$ . No transfer of work is evident to the observer located upon this stationary system, and therefore

$$Q - W = h_{2'} - h_2 + \frac{V_{r'}^2 - V_r^2}{2Jg_c} = 0$$

and

$$h_{2'} - h_2 = \frac{V_r^2 - V_{r'}^2}{2Jg_c}$$

On leaving the blade, the fluid may still have a relatively high velocity. This is reduced by fluid turbulence within the casing and exhaust pipe (with consequent increase in enthalpy), and the leaving velocity is essentially small.

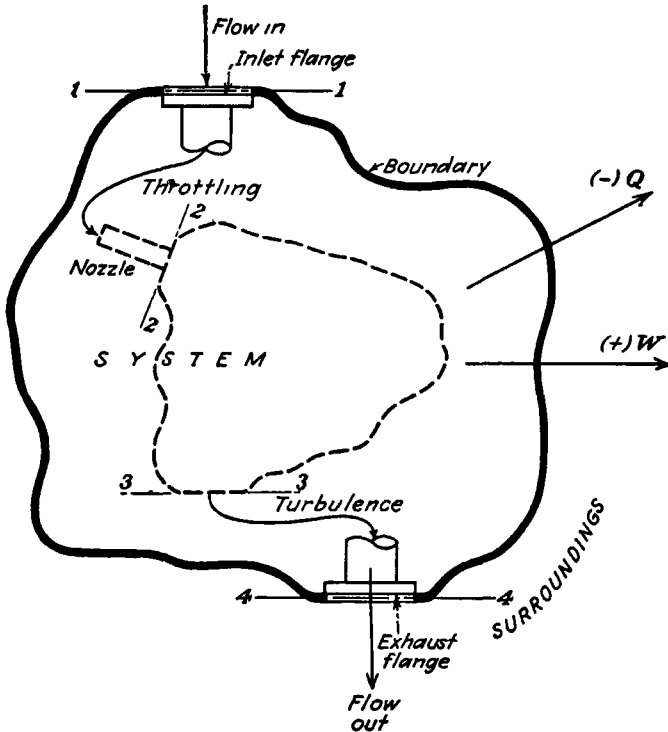


FIG 3-21 Nonadiabatic system for flow through entire turbine

In the same manner as for a blade, Eq (3-13) can be applied to the entire turbine, ignoring entirely the changes taking place within the

system (Fig 3-21)

$$Q - W_{\text{turbine}} = h_4 - h_1 + \frac{V_4^2 - V_1^2}{2Jg_c}$$

Here, whether or not the turbine is of the impulse type is unimportant. Heat transfer for this system represents that unavoidably radiated or conducted to the surroundings. Although the total quantity of heat transferred may be large, the amount per unit mass flow through the turbine is small and can usually be neglected. The velocities of the fluid entering or leaving the turbine are small in value (but not the velocities within the turbine) and also can be neglected.

$$W_{\text{turbine}} = h_1 - h_4 \text{ Btu/lb}_m$$

The question again arises: Is this the maximum work that can be done by the turbine? No decision can be made from the evidence at hand. The work output is merely shown to be the difference between the total energy put in and that taken out of the system, and this relationship will be true for real or ideal machines.

*g Condensers* A surface condenser consists of a shell enclosing a number of tubes in the manner illustrated in Fig 3-22. Cold water is admitted to the water box and then passes through the lower bank of

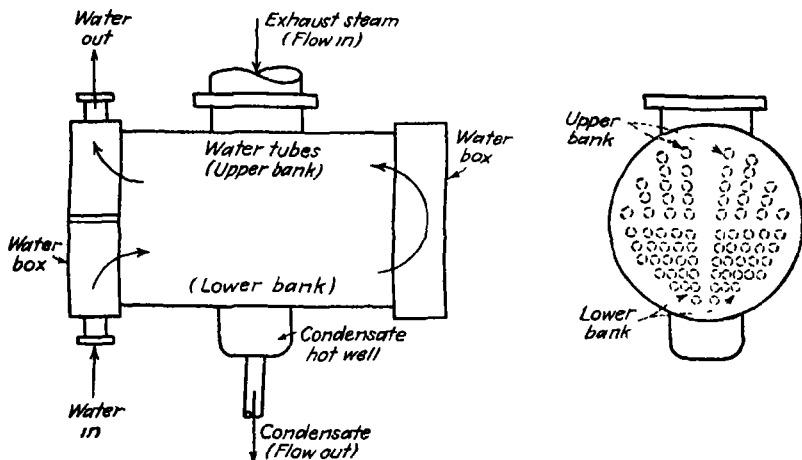


FIG 3-22 Two-pass surface condenser

tubes to the opposite water box. Here it passes upward and back through the upper bank of tubes. This is a *two-pass* condenser. Steam is admitted at the top of the condenser and passes downward over and between the tubes and condenses on the cold surface of the

tubes. The condensate is collected in the *hot well* and pumped back to the boiler. An advantage of a surface condenser is that it permits re-use of the condensed steam as boiler feed water. Since the feed water in many localities must be distilled or treated to prevent deposits in boiler and turbine, the use of a surface condenser will effect a considerable saving in treating costs. Too, the water used for condensing the steam never comes in contact with the condensate and any cheap water supply can be used for cooling the condenser.

Figure 3-23 is a diagrammatic sketch of this system. Equation (3-13) applied to Fig. 3-23 shows that

$$Q = h_2 - h_1 \text{ Btu/lb}_m$$

because

$$V_1 \approx V_2 \quad z_1 \approx z_2 \quad W = 0$$

**3-7. The Power Cycle.** A simple steam power plant is shown in Fig. 3-24. Water is pumped into the boiler by the centrifugal pump

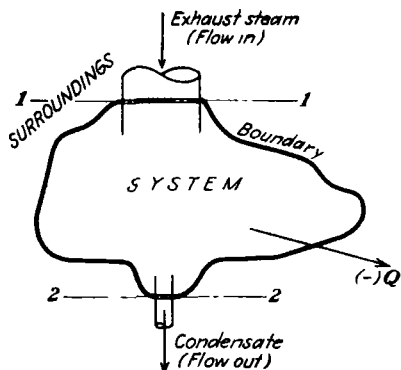


FIG. 3-23 System of surface condenser and single flow path of steam condensate (Flow path of cooling water is in the surroundings)

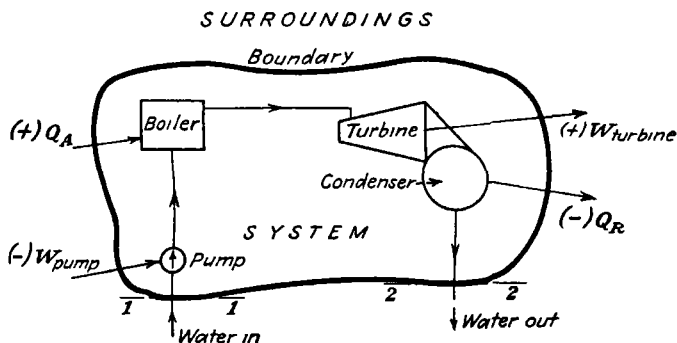


FIG. 3-24 Heat-power cycle open system (single flow path of water)

and is evaporated into steam while heat is supplied at a high temperature. The steam flows through a turbine doing work  $W$  and then passes into a condenser where it is condensed into water. This is a heat-rejection process at a temperature approaching that of the

atmosphere. Examination of the water leaving the system shows that it has the same properties as the water entering the system despite the number of processes that have occurred. The water has gone through a *cycle*.

A cycle is said to occur when the working fluid of a system experiences a number of processes that eventually return the fluid to the initial state.

Applying Eq (3-13) to the open system of Fig 3-24,

$$\Sigma Q - \Sigma W = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2Jg_c} + \frac{g}{Jg_c} (z_2 - z_1) = 0$$

But  $z_1 = z_2$ ,  $V_1 = V_2$  and  $h_1 = h_2$  because the properties of the water entering and leaving the system are the same, and

$$\Sigma Q = \Sigma W$$

where  $\Sigma W$  = turbine work + pump work (pump work is a negative quantity)

Since all power cycles have a heat-rejection process as an invariable characteristic, the work done is always less than the heat *added*, although, as shown above, it is equal to the net amount of heat

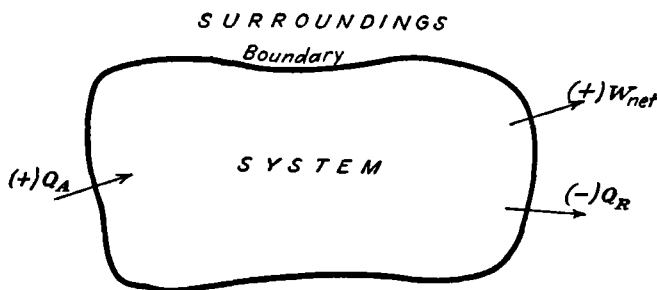


FIG 3-25 Heat-power cycle closed system

Whenever a cycle occurs, an open system can be converted to a closed system. In Fig 3-24 the water leaving the system can be diverted back to take the place of the water entering the system. This new closed system is shown in Fig 3-25. The energy of this system is constant because at any point within the system the conditions or events occurring are always the same (assuming steady-state operation). Equation (3-1) can be directly applied to this closed

system:

$$\begin{aligned}\Sigma Q - \Sigma W &= 0 \\ \Sigma Q &= \Sigma W\end{aligned}$$

which is, of course, the same answer as before.

Most of man's efforts to obtain work from conversion of heat energy have been directed toward improving the efficiency of a power cycle.

**The efficiency of the cycle in producing work from heat is called the thermal efficiency.**

$$\eta_t = \frac{\text{work done}}{\text{heat added}} = \frac{\Sigma Q}{Q_A} \quad (3-19)$$

In many instances, the cycle is not complete; for example, in Fig. 3-24 the condenser could be eliminated and the turbine could exhaust to the atmosphere. Realization that in this case the values for  $Q_A$  and  $W$  are not affected by the change enables the thermal efficiency to be written as

$$\eta_t = \frac{\Sigma W}{Q_A} \quad (3-20)$$

However, incomplete cycles must be carefully examined to ensure that proper values are given to  $\Sigma W$  and  $Q_A$ , else a fictitious value for the thermal efficiency will result. *Obviously, recognition of the cycle is a prerequisite before a cycle efficiency, which is called thermal efficiency, can be calculated.* The power cycle is characterized by a heat-addition process at a high temperature and an inevitable heat-rejection process at a lower temperature. No system has yet been devised that would have a thermal efficiency of as much as 50 per cent, while values of 10 and 20 per cent are more usual. In Art. 3-2 a cycle was devised that completely and continuously converted work into heat. No problem attended this conversion. The reasons for failure to convert heat into work completely and continuously cannot be surmised from the First Law but must be left for a later chapter to explain.

### Problems

#### CLOSED SYSTEM

1. A system receives 100 Btu of heat while work of amount 125 Btu is transferred to the surroundings. Is this possible?
2. A system transfers 100 Btu of heat to the surroundings while receiving 100 Btu of work. What is the name of the process?
3. The energy of a system increases by 50 Btu while 75 Btu of work are transferred to the surroundings. Is heat added or taken away from the system?



4. *a.* The energy of a system increases by 50 Btu while the system is receiving 40 Btu of work. How much heat is transferred and in what direction?

*b.* The energy of a system decreases by 25 Btu while the system is receiving 30 Btu of work. How much heat is transferred?

*c.* During an expansion process, the work transfer is 10 Btu while the heat received by the system is 20,000 ft lb/. What is the change in energy for the system?

5. During a compression process the work transfer is 8,000 ft lb/, while the heat received by the system is 25 Btu. What is the change in energy for the system?

6. A constant-volume system receives heat of amount 10 Btu and work of amount 5 Btu. Find the change in energy.

7. A closed system consists of a cylinder of water and ice stirred by a paddle wheel. For the process the work was 17 Btu hr<sup>-1</sup>, the initial internal energy was 133 Btu, and the final internal energy after one-half hour of stirring was 126 Btu. Find the heat exchange in Btu per hour. Is the temperature of the system rising or falling?

8. A piston-cylinder arrangement has a gas in the cylinder space. During a constant-pressure expansion to a larger volume, the work effects for the gas are 1.60 Btu, the heat added to the gas and cylinder arrangement was 3.17 Btu, and the friction between the piston and cylinder wall amounted to 0.25 Btu. Determine the external useful work done by the process, the change in internal energy of the entire apparatus (gas, cylinder, piston), and the change in internal energy of the gas only.

9. List a number of systems that will continuously and completely convert work into heat.

10. The energy of a constant-volume process increases by 10 Btu while only 5 Btu of heat are added. Was work transferred during this process? Can your statement be proved?

11. An adiabatic compression process involves the transfer of 10 Btu of work. What are the value and direction for the change in energy of the system?

12. Repeat Prob. 11 but assume that the process is one of expansion.

13. An expansion process at constant energy involves the transfer of 10 Btu of heat. Determine the value and direction for the transfer of work.

14. Devise an expansion process at constant energy that would not involve either heat or work.

#### STEADY-FLOW SYSTEM

15. A system has a mass flow rate of 1 lb<sub>m</sub> sec<sup>-1</sup>. The enthalpy, velocity, and height at the entrance are, respectively, 100 Btu lb<sub>m</sub><sup>-1</sup>, 100 ft sec<sup>-1</sup>, 300 ft. At exit these quantities are 99 Btu lb<sub>m</sub><sup>-1</sup>, 1 ft sec<sup>-1</sup>, -10 ft. Heat is transferred to the system of amount 5 Btu sec<sup>-1</sup>. How much work is done by this system (a) per pound of fluid flow, (b) per minute, (c) in horsepower?

16. Repeat Prob. 15, changing the entrance and exit conditions to  $h_1 = 1000$  Btu lb<sub>m</sub><sup>-1</sup>,  $V_1 = 10$  ft sec<sup>-1</sup>,  $z_1 = 100$  ft,  $h_2 = 1030$  Btu lb<sub>m</sub><sup>-1</sup>,  $V_2 = 10$  ft sec<sup>-1</sup>,  $z_2 = 50$  ft.

17. On entering a system the pressure is 100 psia, specific volume 3 ft<sup>3</sup> lb<sub>m</sub><sup>-1</sup>, and internal energy 900 Btu lb<sub>m</sub><sup>-1</sup>. On leaving, the pressure is 90 psia, specific

volume  $4 \text{ ft}^3 \text{ lb}_m^{-1}$ , and internal energy  $850 \text{ Btu lb}_m^{-1}$ . If the process is adiabatic and without change in kinetic or potential energy, how much work can be done?

18. A fluid enters a system with a velocity of  $10 \text{ ft sec}^{-1}$  through a 6-in diameter round pipe. The enthalpy is  $1000 \text{ Btu lb}_m^{-1}$ , internal energy is  $900 \text{ Btu lb}_m^{-1}$ , and the pressure is 100 psia. At exit the enthalpy is  $900 \text{ Btu lb}_m^{-1}$ . If the process is adiabatic while the changes in kinetic and potential energies are negligible, find the rate of work transferred in horsepower.

19. Water enters a boiler with enthalpy of  $60 \text{ Btu lb}_m^{-1}$  and steam leaves with enthalpy of  $1200 \text{ Btu lb}_m^{-1}$ . How much heat was transferred? Define the system.

20. From Fig 3-6 define a system that will allow steam to be generated without flow of heat to your system. What is transferred in this double-circuit flow system? Set up an equation for the system of combustion gases alone in Fig 3-6.

21. Enumerate difficulties in evaluating the storage term of Eq (3-4). How are these difficulties circumvented?

22. From Fig 3-9 define a system that will be essentially adiabatic. How many flow circuits are involved?

23. An air compressor compresses 100 cfm of air with specific volume of  $12 \text{ ft}^3 \text{ lb}_m^{-1}$ , the enthalpy of the air increases  $300 \text{ Btu min}^{-1}$  while the enthalpy of the cooling water increases  $20 \text{ Btu lb}_m^{-1}$  of air delivered. Neglecting changes in kinetic or potential energy, find the horsepower required by the system.

24. A centrifugal air compressor compresses  $5 \text{ lb}_m \text{ min}^{-1}$  of air from an initial pressure of 14.7 psia to a final pressure of 150 psia. The change in enthalpy of the air is  $25 \text{ Btu lb}_m^{-1}$ . How much work is required to drive the compressor?

25. A gas expands in a nozzle with the change of enthalpy equal to  $50 \text{ Btu lb}_m^{-1}$ . What will be the velocity of the fluid if the initial velocity is zero? If the initial velocity is  $100 \text{ ft sec}^{-1}$ , what will be the final velocity?

26. A fluid passes through a device wherein the velocity increases from  $15 \text{ ft sec}^{-1}$  to  $1,000 \text{ ft sec}^{-1}$  without transfers of heat or work. What is the value for the change in enthalpy? The outlet velocity is dissipated by friction and turbulence until the initial value for velocity of  $15 \text{ ft sec}^{-1}$  is regained. What is the value for the change in enthalpy when this condition is reached?

27. As the flow jet passes across a turbine blade without friction, its velocity is reduced from  $1,500 \text{ ft sec}^{-1}$  to  $500 \text{ ft sec}^{-1}$ . How much work can be done by the system of blade and fluid?

28. As the flow jet passes across a turbine blade with friction present, its velocity is reduced from  $1,200 \text{ ft sec}^{-1}$  to  $300 \text{ ft sec}^{-1}$  while the enthalpy increases  $10 \text{ Btu lb}_m^{-1}$ . How much work can be done by the system?

29. The enthalpy of the fluid entering a reaction turbine is  $1000 \text{ Btu lb}_m^{-1}$  while at the exit the enthalpy is  $900 \text{ Btu lb}_m^{-1}$ . How much work can be done by this system if changes in kinetic and potential energies are negligible and the system is essentially adiabatic? How can this problem be solved, since you do not know the sequence of processes or the mechanism within the turbine?

30. Steam enters a condenser with enthalpy of  $1000 \text{ Btu lb}_m^{-1}$ , and condensate leaves the condenser with enthalpy of  $80 \text{ Btu lb}_m^{-1}$ . The cooling-water circuit has a temperature increase from entrance to exit of  $10^\circ$ . If this temperature rise corresponds to an enthalpy increase of  $10 \text{ Btu lb}_m^{-1}$  of cooling water, how many pounds of cooling water are needed to condense  $1 \text{ lb}_m$  of steam?

31. Steam enters a four-pass condenser with enthalpy of  $1000 \text{ Btu lb}_m^{-1}$  and velocity of  $300 \text{ ft sec}^{-1}$ , while the condensate leaves with enthalpy of  $80 \text{ Btu lb}_m^{-1}$

and negligible velocity How much heat must be transferred from the system of steam and condenser? Repeat, assuming a two-pass condenser

**32.** The heat transferred to a power cycle is  $1200 \text{ Btu lb}_m^{-1}$  while the heat rejected is  $800 \text{ Btu lb}_m^{-1}$  and the pump work is  $5 \text{ Btu lb}_m^{-1}$  What is the value for thermal efficiency? *Ans  $\eta_t = 33\frac{1}{3}$  per cent*

**33.** The heat rejected from a power cycle is  $400 \text{ Btu lb}_m^{-1}$ , while the work done by the turbine is  $200 \text{ Btu lb}_m^{-1}$  and the pump work is  $5 \text{ Btu lb}_m^{-1}$  Calculate the thermal efficiency

**34** Fluid enters a turbine with velocity of  $5 \text{ ft sec}^{-1}$  and enthalpy of  $900 \text{ Btu lb}_m^{-1}$  and leaves with enthalpy of  $800 \text{ Btu lb}_m^{-1}$  and velocity of  $300 \text{ ft sec}^{-1}$ , while the heat loss is  $30 \text{ Btu min}^{-1}$  and flow rate is  $1 \text{ lb}_m \text{ sec}^{-1}$  What horsepower will be developed?

**35.** The absolute velocity of the fluid leaving the nozzle is  $1,000 \text{ ft sec}^{-1}$ , and the velocity of the blade is  $500 \text{ ft sec}^{-1}$

*a* If the angle of the nozzle to the blade is  $12^\circ$ , what angle will the relative velocity vector make to the axis of the blade (graphical solution)?

*b* Suppose the fluid leaves the blade with a relative velocity only  $0.9$  that of the entering relative velocity What will be the value for the work done by the blade?

*c* If no friction is present, how much work will be done?

**36.** Water is drawn from a lake, pumped up to a city  $486 \text{ ft}$  above lake level, and forced through the nozzles of a fire hose at  $64 \text{ ft sec}^{-1}$  Neglecting friction, what horsepower is theoretically needed to deliver  $5,000 \text{ lb}_m \text{ sec}^{-1}$  of water?

### Symbols

<i>A</i>	area
<i>F<sub>c</sub></i>	correction factor for nozzle
<i>D</i>	diameter
<i>E</i>	energy in general
<i>e</i>	energy in general per unit mass (specific)
<i>F</i>	friction, turbulence, throttling
<i>g</i>	local acceleration of gravity
<i>g<sub>c</sub></i>	dimensional constant
<i>h</i>	enthalpy per unit mass (always in thermal units) (specific)
hp	horsepower
<i>J</i>	Joule's equivalent
<i>L</i>	length, distance
<i>m</i>	mass, also, mass flow rate
<i>p</i>	pressure
<i>Q</i>	heat
<i>U</i>	internal energy (always in thermal units)
<i>u</i>	internal energy per unit mass (always in thermal units) (specific)
<i>V</i>	velocity, also, volume
<i>v</i>	specific volume
<i>W</i>	work
<i>w</i>	weight of mass <i>m</i>
<i>z</i>	height
$\approx$	approaches equality

**Greek Letters**

$\eta$	(eta)	thermal efficiency
$\delta$	(delta)	infinitesimal change
$\Delta$	(delta)	finite change
$\Sigma$	(sigma)	summation

**Subscripts**

$A$	added
$b$	blade
$f$	force
$m$	mass
$r$	relative







## CHAPTER IV

### THE REVERSIBLE PROCESS

In his search for the most efficient way to produce work from heat, the engineer must examine each process for imperfections. From experience he has found it easy to convert work into heat but impossible to convert heat into work completely and continuously. For this reason he must avoid processes that allow work, or even a latent capability to do work, to be dissipated in friction or turbulence.

**4-1. Available Energy.** Not all of the energy contained or associated with mass can be converted into work even under ideal conditions, but only a fraction of the absolute quantity is available for use. This fraction is called the *available energy*,<sup>1</sup> and the remainder, *unavailable energy*.

**Available energy in the broadest sense of the term is the maximum amount of work that can be obtained from a quantity of energy in a specified state.**

Consider a system containing energy in many different forms. Assume that this system is to be used as a reservoir of energy, then, the various types of energy would be available for doing work if the potential properties for these forms of energy were greater than those of the ultimate reservoir for all systems, the earth and its atmosphere (Here the word *atmosphere* implies the rivers and lakes as well as the air of the earth). For, if a difference in potentials exists between the reservoir and the earth, energy in the form of work can be abstracted from the reservoir. But when the potentials of the reservoir are equal to those of the earth, no further transfer of energy is possible, and, although the reservoir contains energy, this energy is unavailable for doing work. In this respect, kinetic and potential energies can be considered to be fully available, if only because the values for these forms of energy are computed above an arbitrary datum that is the surface of the earth. If, for example, the datum of zero potential energy were to be established at the center of the earth, potential energy would be, to a great extent, unavailable energy. Similarly,

<sup>1</sup> It is also called the *availability* (Art 12-13)



the potential of pressure enables the system to expand and therefore do work by virtue of its internal energy, but such expansion cannot be continued to an absolute zero of pressure because the atmosphere of the earth exerts an essentially constant restraining pressure ( $p_0$ ). If expansion is to proceed past the practical datum of atmospheric pressure, work cannot be obtained but must be supplied by some other system.

When the reservoir involves a flow process, the defined form of energy called *flow energy* (Art 2-9) must also be considered even though the source of the flow energy lies in some other system. Nevertheless, the flow energy of the stream is available to do work and should properly be included as a part of the available energy of the system. Here, as in the case of expansion energy, the available part of flow energy is that over and above the energy necessary to overcome the pressure of the atmosphere (note Art 4-6).

Thus, the term *available energy* denotes the latent capability of a quantity of energy to do work, and in this sense it can be applied to energy in the system and, also, to energy in the surroundings, for it should be realized that the surroundings are but another system. Moreover, the term will often be used as a synonym for work, especially for cases where the boundary is not well delineated.

But a portion of heat energy could also quite properly be called available energy because work can be produced from heat, and the term available energy, when used with the broadest possible meaning, must include the available part of heat energy. The available part of heat energy, for simplicity of expression, will also be called the *availability* of heat. The evaluation of the maximum amount of work that can be obtained by transformation of heat, the availability of heat, will be made in Chap V. Here it is sufficient to note that the temperature of the earth ( $t_0$ ) again imposes a lower limit to the abstraction of energy in the form of the heat from a reservoir of energy.

**4-2. The Perfectly Performed Process.** Work must be a more precious form of energy than heat because experience shows that only a fraction of the heat supplied to a cycle can be transformed into work. Evidently, the clue to perfection of a process is to ensure that work is not being used to effect a change that could be as readily attained by transfer of the cheaper commodity, heat.

**A process is ideally performed when neither work nor available energy is used to cause a change that could have been accomplished in whole or in part by transfer of heat.**

**4-3. The Concept of Reversibility.** From experience it is observed that work is more adaptable than heat. To accomplish the same objective as a transfer of heat, work can always be substituted for heat (turbulence and frictional effects). But when a change is accomplished by transfer of work, heat cannot be substituted for the work. It then follows immediately that, if any process is stopped and made to retrace its steps by returning to the system the work and heat previously delivered, only the perfect process can do this and regain the original state.

**If a process is reversible, neither work nor available energy has been used for purposes that could have been served by transfer of heat.**

**A perfectly executed process is a reversible process.**

In many cases it is convenient to test for imperfections by noting whether a process can be reversed. In other cases it should be remembered that reversibility is merely a test to ensure that neither work nor available energy is misused. In Art. 3-2 work was added to a constant-volume system to change its state, clearly this is an irreversible process because no means can be devised whereby cooling the system could rotate the paddles and deliver back to the surroundings the *same amount*<sup>1</sup> of work as was originally supplied. The process is undesirable either by the concept of reversibility or by noting that work is used for a change that could have been produced by transfer of heat.

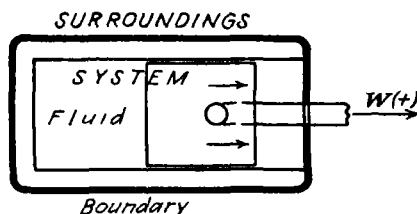


FIG 4-1 Adiabatic system of fluid, piston, and cylinder (Cross section resembles that of an air compressor or a gasoline or steam engine)

It will be well to examine instances where irreversibilities occur in order to note certain characteristics of the reversible process. In Fig. 4-1 is shown an adiabatic system that consists of working fluid and mechanical parts. The fluid is slowly expanding in the cylinder and exerting a pressure on the piston. If mechanical friction is present between piston and cylinder or in any other device within the system, the net work delivered by the system will be less than a possible maximum because part of the available energy is dissipated by the

<sup>1</sup> Thermal currents, however, on cooling might rotate the paddles and so deliver a very small amount of work.

**friction** If friction is not present, the process can be reversed and the original state can be regained by returning to the system the work previously delivered to the surroundings. In this case the system and surroundings are returned to their original states, and therefore the process is reversible.

**A reversible process, when undone, will leave no evidence of the events in the surroundings.**

Evidently it is correct to say that a reversible process is a frictionless process. Conversely, an expansion process with friction is an irreversible process and obviously delivers less work (and requires more work for the inverse process of compression) than the corresponding reversible process. For the system of Fig 4-1 assume that after the frictional (but adiabatic) process the system is to be reversibly returned to its initial state. To do this the system must first be cooled by transfer of heat until the internal energy is equal to that remaining after the reversible process. Since less work is done by the irreversible process, more energy must remain in the system. Now assume that the friction is eliminated and the system is reversibly compressed back to its initial state. For these hypothetical conditions, collecting all heat and work transfers between system and surroundings shows that, because the system is restored to its initial state,

$$\begin{aligned} Q - \Sigma W &= \Delta E = 0 \\ Q &= \Sigma W \end{aligned}$$

Although, as to be expected from the First Law, no loss of energy is experienced by the surroundings, it is found that the surroundings had to supply work and accept heat as payment, clearly, this is not a fair exchange.

**An irreversible process when reversibly restored to its original state will leave a history of the events in the surroundings. The history in every case will reveal an exchange of heat for the more precious form of energy, work.**

As a second step in the investigation of the meaning of the concept of reversibility, consider the adiabatic system of fluid alone in Fig 4-2. If the piston moves at a slow speed, the same pressure will exist at any instant in all parts of the chamber, and the maximum amount of work will be done on the piston. Now assume that the piston moves at a rate such that a pressure difference is caused to exist between chambers A and B. A lower pressure will be exerted on the piston than was

experienced before, and a lesser amount of work will be done. In the first process, the piston may be stopped at any time and reversed, the gas being compressed from state to state in the exact inverse order of the original expansion. This is a reversible process.

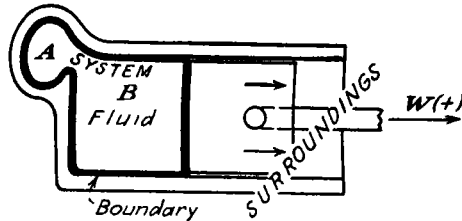


FIG 4-2 Adiabatic system of fluid alone (Cross section resembles that for a precombustion chamber diesel engine)

**A reversible process must pass through the same states on the reversed path as were initially visited on the forward path.**

The fluid in the irreversible expansion process was highly turbulent because of the variation in pressure. Definition of a single state for the system was impossible because the properties defining the state were not uniform throughout the fluid.

**A reversible process must pass through a continuous series of equilibrium states.**

This statement requires that the process must proceed at an infinitely slow pace if all potentials of the system are to be in balance with the surroundings and internally in balance throughout the system.

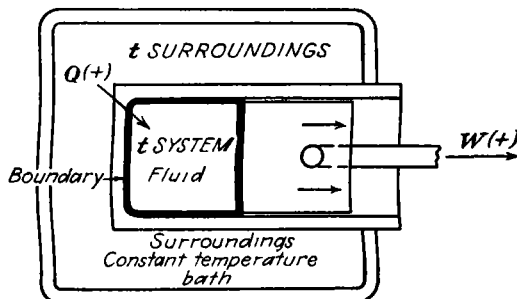


FIG 4-3 Isothermal system of fluid alone

It should now be apparent that reversibility is a test for the absence of internal turbulence of the working fluid as well as for the absence of mechanical friction of the mechanism. Even so, the picture is not complete, for reversibility is a much broader concept. As the third

step in this investigation, consider the system of fluid alone in Fig 4-3. Here a gas is expanding while heat is being supplied at a rate such that the temperature of the gas remains constant. If the piston moves at a very slow speed, the temperature difference between system and surroundings can be made extremely small and considered to approach zero. Then, at any stage of the expansion, the process can be reversed and heat transferred from the system by supplying the work that was previously transferred to the surroundings. The process is reversible. If the temperature difference is greater than zero, this reversibility is not possible because insufficient work will be available to restore the piston.

That a temperature difference will prevent the attainment of the maximum work can be understood from the following argument. A reversible and an irreversible expansion process are receiving heat from the same temperature source. For the reversible process the transfer of heat is taking place with an infinitesimally small temperature difference between source and system. For the irreversible process the transfer of heat is taking place across a finite temperature difference. Then at any stage of the expansion, the fluid in the irreversible process will be at a lower temperature than that in the reversible system, and therefore the pressure will be lower. The work done by the irreversible process will be less than that done by the reversible process. Similar reasoning shows that more work will be required for the irreversible compression process to achieve the higher temperature necessary to establish a temperature difference between the system and reservoir.

**For a reversible process, heat must be transferred only through an infinitely small temperature difference.**

A more general indication can be given that a temperature gradient is undesirable. In Fig 4-4a, a finite temperature difference exists between the source  $A$  and the system  $C$  which undergoes a cycle. The thermal efficiency of the cycle is

$$\eta_{ic} = \frac{\Sigma W}{Q_A} = \frac{Q_A + Q_R}{Q_A} = 1 + \frac{Q_R}{Q_A} \quad (a)$$

( $Q_R$  is a negative quantity.) Now suppose another cycle, system  $B$ , is inserted between  $A$  and  $C$  as shown in Fig 4-4b. Let heat of amount  $Q'_A$  be reversibly transferred to  $B$  while the heat rejected from  $B$ , of amount  $Q_A$ , is reversibly transferred to system  $C$ . (To effect these reversible transfers of heat, no finite temperature differences can

exist, and therefore the processes must proceed at an infinitely slow pace) But the thermal efficiency for this combination of systems *B* and *C* is

$$\eta_{(B+C)} = \frac{\Sigma W}{Q'_A} = \frac{Q'_A + Q_R}{Q'_A} = 1 + \frac{Q_R}{Q'_A} \quad (b)$$

In comparing Eqs (a) and (b) note that  $Q_R$  has the same (negative) value for either equation, and  $Q'_A$  is larger than  $Q_A$ . Therefore, the efficiency of cycles *B* plus *C* is greater than the efficiency of cycle *C* alone. The temperature difference between *A* and *C* could have been

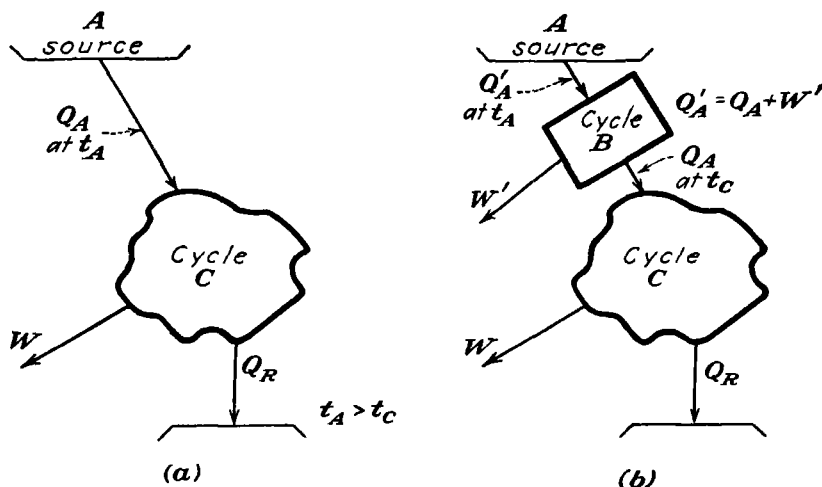


FIG 4-4 Effect of a temperature difference on thermal efficiency

utilized to obtain work but, instead, was used to hasten the transfer of heat (and haste may be well worth this cost). Nevertheless, the argument shows that heat transferred through a temperature difference is an irreversibility that prevents the attainment of the maximum thermal efficiency.

All the examples have emphasized that reversible processes can be stopped at any instant and restored to their original states. This concept is more difficult to visualize when applied to open systems under steady flow where kinetic effects usually lead to irreversibilities. Despite this difficulty all such processes, if reversible, can be undone so as to leave no trace of the events in the surroundings. Consider the nozzle wherein pressure decreases and velocity increases, by leading the high-velocity fluid through a *diffuser* the velocity can be reduced and pressure increased. A diffuser is merely a reversed

nozzle but of longer length as illustrated in Fig. 4-5. The combination of nozzle and diffuser is called a *venturi*.

It is helpful to divide the irreversibilities present in a system into two classes, *internal* and *external*. An *internal irreversibility* is any factor present within the system that prevents the attainment of a state of equilibrium, such as turbulence or the presence of any potential gradient. An *external irreversibility* is a factor present at the boundary of the system, such as mechanical friction or a temperature difference. By redefining the system, external irreversibilities can be made part of the surroundings, and the new system may approach reversible operation (if further

internal irreversibilities are absent)

To achieve reversible operation, a process must proceed at an infinitely slow pace, and finite speed of operation prevents attainment of the ideal (while the slow pace, in itself, would certainly be impractical

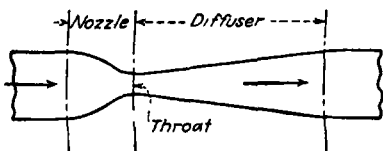


FIG 4-5 Venturi

in this world of haste). Certain processes, however, can approach reversible operation while others can by no means be rationalized to show reversibility. The task of the engineer is to recognize and evaluate the factors preventing complete reversibility and to select for purposes of power those processes that, if not reversible, at least have adequate justification for the irreversibilities that may be present.

**4-4. Work and the Closed System.** The work of expansion for a closed system that is initially in a state of equilibrium is derived entirely from the potential of pressure moving the boundary against a resistance furnished by the surroundings. For the more general case, the pressure is not constant during the process but has different values as the expansion or compression proceeds. The maximum<sup>1</sup> work will be realized when the process is conducted reversibly. For any expansion or compression process the work can be evaluated by

$$W = \text{force} \times \text{distance}$$

The force arises from the pressure of the system acting upon a movable area of the boundary; force equals pressure times area. This area will be forced through a distance  $L$  against the resistance of the surroundings, and the work obtained is

$$W_{\text{rev}} = \int p A \times dL$$

nonflow

Integration is necessary because pressure is not necessarily constant

<sup>1</sup> Or the minimum work for compression

But  $AdL$  is  $dV$ , the change in volume, and therefore

$$W_{\text{rev nonflow}} = \int_{V_1}^{V_2} p dV = m \int_{v_1}^{v_2} p dv \quad (4-1)$$

*This is the work of a reversible process from the potential of pressure in a closed system.* To evaluate this expression, the relationship between pressure and volume must be determined for the process under conditions of reversibility.

To study a process, it is convenient to show the change on a diagram that has properties as coordinates. The  $pv$  diagram (Fig 4-6) is important because the area under the pressure-volume path *may be* work, for this area is  $\int p dv$ . Since each state on the diagram presupposes an equilibrium state, a continuous path (1-2) can be rigorously<sup>1</sup> interpreted only as an internally reversible process. This is not as serious a restriction as it might seem. For fluids compressed or expanded within a cylinder by a piston the internal irreversibilities may be quite negligible. However, for fluids compressed by centrifugal means the  $pv$  diagram should be used only to show the initial and final states. These two states can be located and connected by a dashed line (1-3) to indicate the uncertainty of the path, for in such processes there may be finite differences in pressure, temperature, specific volume, and other properties, and a single state for the system is impossible to define. In other cases of irreversibilities it may be possible to stop the process (if only in imagination) at frequent intervals and so attain an equilibrium state. The path can be approximated in this case by connecting the known (or imagined) equilibrium states (1-4).

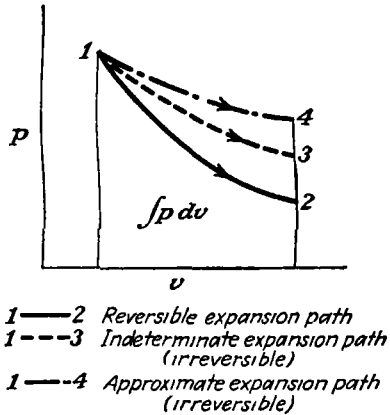


FIG 4-6 Pressure specific-volume ( $pv$ ) diagram

**Example 1.** During a reversible and nonflow expansion process the pressure and specific volume are observed to be related by the relationship

$$pv^2 = C \text{ (constant)}$$

Derive a formula for the work done

<sup>1</sup> Real processes, however, that approach reversibility will be shown as solid lines in subsequent figures



Solution :

$$W_{\text{rev}} = \int p dv$$

and

$$p = \frac{C}{v^2}$$

$$W_{\text{rev}} = C \int_{v_1}^{v_2} \frac{dv}{v^2} = C \left( -\frac{1}{v} \right)_{v_1}^{v_2}$$

$$W_{\text{rev}} = C \left( \frac{1}{v_1} - \frac{1}{v_2} \right) = pv^2 \left( \frac{1}{v_1} - \frac{1}{v_2} \right) = p_1 v_1 - p_2 v_2 \quad \text{Ans}$$

**4-5. The Engine Indicator.** In the laboratory, the pressure in the cylinder of a large, slow-speed engine may be found by using an indica-

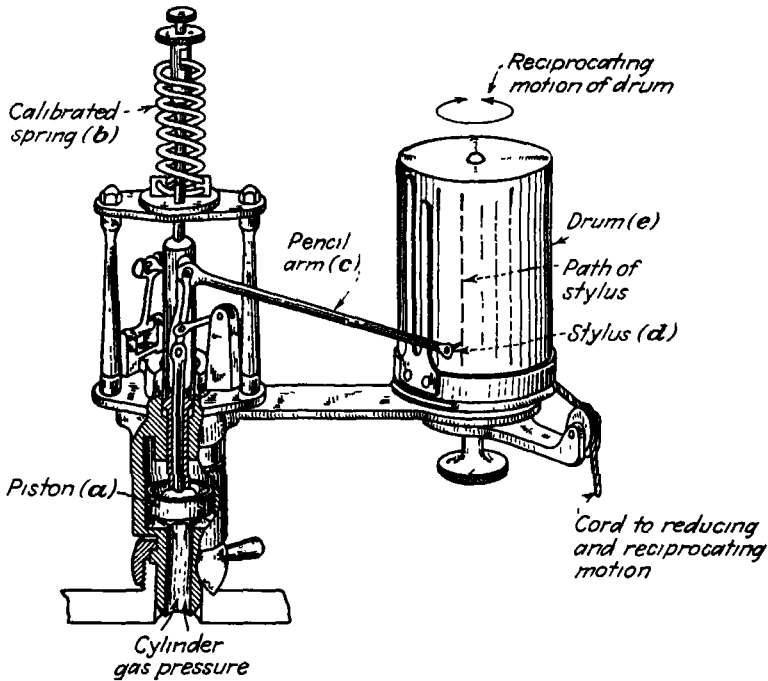


FIG 4-7 Engine indicator

tor such as illustrated in Fig 4-7. The indicator can be attached to the engine cylinder to allow the gas pressure to be applied against the piston *a*. Attached to this piston is a calibrated spring *b*. The vertical movements of the indicator piston, caused by pressure changes in the engine cylinder, are multiplied through the pencil-arm mechanism *c*. This motion is indicated by the stylus *d*, which marks the pressure on a card mounted on the drum *e*. By use of a suitable reducing

motion driven by the engine, the drum can be given a reciprocating motion proportional to the movement of the engine piston. In operation the drum oscillates in time with the engine piston while the stylus moves through vertical distances proportional to the cylinder pressures and thereby draws a pressure-volume ( $pV$ ), but not specific-volume ( $pv$ ), diagram. Whether the engine process is reversible or not, the indicator, if precise, will draw a diagram exactly proportional to the work done *by the fluid* (as explained in the next paragraph) if the pressure on the indicator piston is the same as that on the engine piston. For the usual locations where the indicator is tapped into the cylinder, even the fastest engines<sup>1</sup> will not create a significant pressure difference between indicator and engine piston.

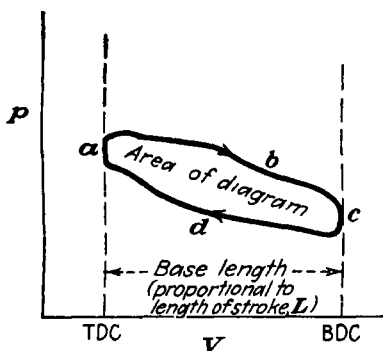
In Fig 4-2, if the indicator is attached to chamber *A*, the work done obviously cannot be determined from the chart because the work bears no simple relation to the pressure experienced by the piston. But if the indicator is connected to chamber *B*, so that the pressure measured is that exerted on the engine piston, the exact work done by the fluid can be determined by measuring the area under the trace drawn by the indicator. The reason it can be determined thus is that the chart is merely a measure of force times distance (because pressure times the area of the piston in the engine is force while the base of the diagram is proportional to the stroke of the engine, or distance traversed by the piston). Nevertheless, the properties of the system cannot be portrayed by the  $pV$  diagram of the indicator (for the system of Fig 4-2) because the system properties are nonuniform during this highly irreversible process: the pressure varies, the specific volume also varies, and the temperature of the fluid is lower near the walls than in the center of the cylinder. These nonuniformities in the properties are magnified by the pressure difference between chambers *A* and *B*. In summary, then, though the work of the irreversible process can be measured by the  $pV$  diagram quite accurately, the process cannot be shown on a  $pv$  diagram with an accuracy reasonably approximating that possible for the reversible process.

In many instances the pressure throughout the entire system can be considered essentially uniform (as in Fig 4-3). Here the pressure can be accurately measured by an indicator, and it will be a property of the entire system. Since the volume and the mass of fluid within the cylinder can be measured, then the average specific volume of the

<sup>1</sup> But too rapid pressure changes cannot be measured because the inertia of the moving parts of the indicator will cause the stylus to overrun. However, electrical measuring equipment can be used to overcome this difficulty.

fluid also can be computed. A path can be drawn on a property diagram of *pressure* and *average specific volume* that will approximate a reversible path, at least within the accuracy of the measuring equipment. In this case, as in the other, a precise indicator measures the *indicated work* of the fluid quite accurately, but here, unlike the other case, the diagram can also be construed to be a diagram of properties as well, pressure and average specific volume.

The indicator is usually attached to a reciprocating-piston engine



TDC-Top dead center (inner limit of piston stroke)

BDC- Bottom dead center (outer limit of piston stroke)

FIG 4-8 Pressure volume ( $pV$ ) indicator diagram

Fig 4-8) Here, as before, an average pressure can be computed for the stroke, but here the pressure opposes the motion of the piston. Note that, whenever a change occurs in the direction of movement of the engine piston, a change must also occur in the algebraic sign of work. In Fig 4-8, whenever the volume increases, work is done by the fluid; whenever the volume decreases, work is done on the fluid. Since the pressure within the cylinder cannot be discontinuous, the pressure-volume diagram must form an area that will be complete when the fluid within the cylinder is restored to the initial state that marked the beginning of the diagram. Figure 4-8 shows that the difference in work areas will equal the enclosed area of the

Now, when the fluid expands in the cylinder of the engine, the pressure is recorded by the indicator at each stage of the piston travel ( $abc$  of Fig 4-8). If the area under this trace is divided by the length of the base and multiplied by the spring scale<sup>1</sup> of the indicator, the average pressure exerted during the expansion stroke can be computed. When a different process is followed in restoring the piston to its original position, a different sequence of pressures is traced, and for this reverse stroke of the piston the indicator drum will also reverse its direction ( $cda$  of

<sup>1</sup> The spring scale is related to the strength of the spring, the size of the indicator piston, and the multiplying factor of the stylus. It is expressed in units of pressure per inch. Thus, a spring scale of 50 means that an increase in pressure of 50 psi will cause the stylus of the indicator to move through a vertical distance of 1 in.

**diagram** Instead of determining the average pressure for each stroke of the piston, the enclosed area of the diagram is measured, and a net average pressure is calculated. The net average pressure for the diagram is called the *indicated mean effective pressure* for the diagram, and it is the algebraic sum of the average pressures for each stroke of the piston.

$$p_{im} = imep = \frac{\text{closed area of diagram}}{\text{length of base}} \times \text{spring scale}$$

The indicated mean effective pressure can be defined as that constant pressure that, by acting alone<sup>1</sup> throughout one stroke, can perform the same amount of work as the varying pressures do in the complete cycle of strokes. Thus, the indicated work of one diagram is

$$\begin{aligned} W_{ind} &= (imep) (\text{area of piston}) (\text{length of stroke}) \\ &= p_{im} AL \end{aligned}$$

The product  $AL$  is called the *piston displacement*  $V_D$ , and for one diagram

$$W_{ind} = p_{im} V_D$$

(The usual units are  $p_{im}$  in  $\text{lb}_f \text{ in}^{-2}$ ,  $V_D$  in  $\text{in}^3$ ; and  $W_{ind}$  in  $\text{ft lb}_f$ .)

Of course, the work done by the engine, the shaft work, will be less than the indicated work because of friction between piston and cylinder and other moving parts of the engine. Conversely, if the engine is driven in the manner of an air compressor, the indicated work will be less than the shaft work that must be supplied. In either case the difference between the indicated and the shaft work is the friction work (note that the algebraic sign of  $W_{friction}$  is always positive)

$$W_{ind} = W_{shaft} + W_{friction}$$

**4-6. Work and the Steady-flow Open System.** In the absence of kinetic and potential forms of energy, the work of the steady-flow process from the potential of pressure can be determined as follows. In Fig 4-9 are shown a piston and cylinder constructed with zero clearance.<sup>2</sup> With all processes reversibly conducted suppose that unit mass of fluid with pressure  $p_1$  enters the cylinder (which is the system) through partition or valve at  $A$  and pushes the piston down-

<sup>1</sup> Here the restraint of the atmospheric pressure can be ignored because in the real engine there will always be two or a multiple of two strokes in each cycle of the mechanism. The work done in pushing back the atmosphere on the expansion stroke is regained when the atmosphere pushes against the piston on the return stroke.

<sup>2</sup> See Art 3-6b

ward to  $B$  \*. After closing the valve let the fluid expand to a lower pressure  $p_2$  while pushing the piston to position  $C$  (Heat can be transferred if desired) As a final step, the valve at  $D$  is opened and the fluid pushed out of the system During these processes assume

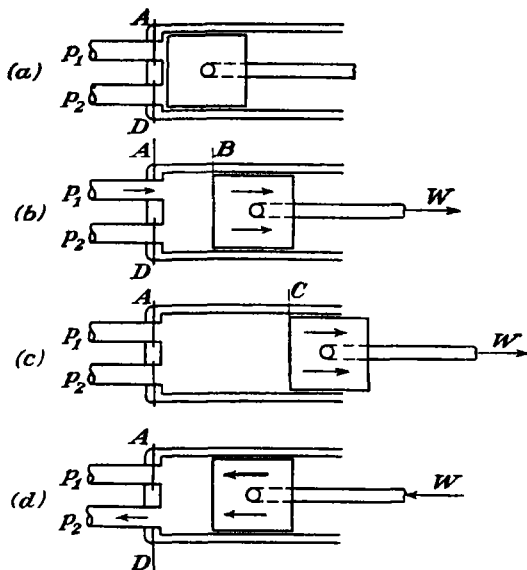


FIG 4-9 Hypothetical flow system (The cylinder marks the extent of the system)

that the piston is connected to an external mechanism so that work is reversibly transferred to the surroundings The pressure-volume sequence during these reversible operations is illustrated in Fig 4-10

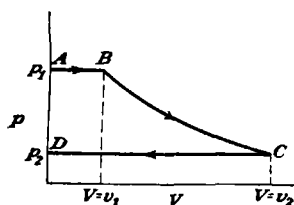


FIG 4-10 The  $pV$  diagram for the system of Fig 4-9

For steady-flow operation a battery of cylinders can be connected by common intake and exhaust pipes, flow into and out of the system will then be at a constant rate The work done by this system for each unit of mass flow will be

$$W = p_1 v_1 + \int_{v_1}^{v_2} p dv - p_2 v_2$$

But from Fig 4-10 (with each area evaluated as a positive quantity)

$$p_1 v_1 + \int_{v_1}^{v_2} p dv = p_2 v_2 + \int_{p_2}^{p_1} v dp$$

\* This operation enables the available part of flow energy to be obtained as work

Transposing,

$$\int_{p_1}^{p_2} v dp = \int_{v_1}^{v_2} p dv - p_2 v_2 + p_1 v_1 = - \int_{p_1}^{p_2} v dp$$

and

$$W_{\text{rev}} = - \int_{p_1}^{p_2} v dp$$

The work of the steady-flow process is the sum of the work done in the many cylinders of the entire system. In each individual case, the same amount of work will be realized. Summation of the work for all the cylinders yields

$$W_{\text{rev flow}} = -m \int_{p_1}^{p_2} v dp \quad (4-2)$$

where  $m$  = mass of fluid entering (or leaving) the system

If potential and kinetic energies are present, mechanisms must be invented to obtain work from these effects before the fluid enters the cylinder of Fig. 4-9 (or after the fluid enters some other system than the simple system of Fig. 4-9). The limit to the transformation of energy into work is per unit mass of fluid flow:

$$W_{\text{rev flow}} = - \int_{p_1}^{p_2} v dp - \Delta KE - \Delta PE \quad (4-3a)$$

This can also be written to show more clearly the forms of energy that were converted into work

$$W_{\text{rev flow}} = \int_{v_1}^{v_2} p dv - \Delta FE - \Delta KE - \Delta PE \quad (4-3b)$$

Inspection of Eq. (4-3b) shows that *the work of the flow process is obtained from four types of energy: expansion or compression energy, flow energy, kinetic energy, and potential energy*. Now recall that, for the nonflow process,

$$W_{\text{rev nonflow}} = \int p dv \quad (4-1)$$

Comparison of Eq. (4-1) and (4-3b) shows that the flow process merely supplements the expansion energy of the fluid with the forms of energy that accompany flow.

**4-7. Heat Capacities.** The concept of reversibility allows the First Law to be expanded to show that the effect of a reversible transfer of heat is indicated by the internal properties of the fluid that are common to both the flow and the nonflow processes. Consider first a nonflow, constant-pressure process. Here the heat required for a

change of state was found to be (Art 3-2c),

$$Q = u_2 - u_1 + W$$

By restricting this process to be a reversible process the work is

$$W_{\text{rev}} = \int p dv = p(v_2 - v_1)$$

and therefore

$$Q_{\text{rev}} \Big|_{p=c} = u_2 - u_1 + p_2 v_2 - p_1 v_1$$

But the combination of properties,  $u + pv$ , is by definition the enthalpy  $h$  (Art 2-11) Thus, *enthalpy is not a property that is restricted only to flow systems:*

$$Q_{\text{rev}} \Big|_{p=c} = h_2 - h_1 \quad (4-4)$$

Equation (4-4) can also be derived for the constant-pressure and reversible flow process Equation (3-12) shows that

$$Q - W = \Delta u + \Delta FE + \Delta KE + \Delta PE$$

and, upon substituting Eq (4-3b),

$$W_{\text{rev}} = \int p dv - \Delta FE - \Delta KE - \Delta PE$$

it will be found that

$$Q_{\text{rev}} = \Delta u + \int p dv$$

and therefore, as in the nonflow process,<sup>1</sup>

$$Q_{\text{rev}} \Big|_{p=c} = \Delta h \quad (4-4)$$

Thus, the heat transferred to a *reversible flow* process is exactly equal in amount to the heat transferred in the similar *reversible nonflow* process The effect of the transfer of heat is reflected by a change in the internal properties of pressure, volume, and internal energy but not in the external properties of velocity and elevation This result could have been anticipated, for, as discussed in Art 2-5, the properties of the quiescent fluid are entirely independent of the properties of velocity and elevation Since the process is reversible, none of these

<sup>1</sup> Note that, by the First Law, the heat transferred to a flow system where work and changes in kinetic or potential energy are zero is

$$Q_{\text{rev or irrev}} \Big|_{\substack{W=0 \\ \Delta KE=0 \\ \Delta PE=0}} = \Delta h$$

But here, if the pressure is constant, the process *must* also be reversible

external forms of energy are dissipated in friction, and thus all thermal effects are derived solely from transfer of heat

For *any* reversible process that does not involve a change of phase, a *heat capacity*, also called *specific heat*, can be defined by

$$Q_{\text{rev}} = m \int_{t_1}^{t_2} c_x dt \quad (4-5)$$

where  $m$  = mass of system

$c_x$  = heat capacity of the fluid for process  $x$

$t_2 - t_1$  = change in temperature for the process

The terms *heat capacity* and *specific heat* are unfortunate names because the quantity  $c_x$  will be shown to be a property that can be changed by other means than transfer of heat. Consider the constant-pressure process. Here Eq (4-4) shows that

$$Q_{\text{rev}} \Big]_{p=C} = m \int dh$$

and, also by Eq (4-5),

$$Q_{\text{rev}} \Big]_{p=C} = m \int c_p dt$$

Therefore,

$$\begin{aligned} dh &= c_p dt \\ c_p &= \left( \frac{dh}{dt} \right)_p = \left( \frac{\partial h}{\partial t} \right)_p \end{aligned} \quad (4-6)$$

In Eq (4-6),  $c_p$  is a function only of properties, then,  $c_p$  is a property that is independent of the external effects of the system, heat and work. For this reason, Eq (4-6) can be used to determine, for example, a change in enthalpy for an irreversible process or for any process that begins and ends at the same pressure. However, in such cases, the change in enthalpy is not equal to the heat transferred, and the value of  $c_p$  must have been previously determined from measurements made under the stipulated restrictions of constant pressure. (It should be recalled that, since the value of a property is determined by the state, the change in value of a property between two states is independent of the process.)

Of the infinite number of heat capacities that could be evaluated, only those for the processes at constant pressure and constant volume are of major importance. The heat capacity at constant volume shows that

$$Q_{\text{rev}} \Big]_{v=C} = m \int c_v dt = m \int du$$



and it equals

$$c_v = \left( \frac{du}{dt} \right)_v = \left( \frac{\partial u}{\partial t} \right)_v \quad (4-7)$$

The amount of heat added to a constant-pressure process must be greater than that necessary to cause the same rise in temperature for a constant-volume process because the fluid expands and work can be done. Then,  $c_p$  must always be larger than  $c_v$ .

Although the heat capacity is a function of both temperature and pressure, the effect of pressure can, in many cases, be ignored. For example, in Fig 1A (Appendix), values for  $c_p$  and  $c_v$  for air are shown along with the ratio  $k$ , defined as

$$k = \frac{c_p}{c_v} \quad (4-8)$$

For temperatures above 400 F the effect of pressure on  $c_v$  is almost imperceptible (at least for air). It then follows immediately from Eq (4-7) that the internal energy of air is primarily a function of the temperature. This conclusion is true for all temperatures above 0 F if the pressure is not high—a fact first noted by Joule (Art 3-2f). The effect of pressure on the heat capacities of gases other than air is illustrated in Fig 1B (Appendix).

TABLE 4-1 —HEAT CAPACITIES OF GASES AT LOW PRESSURES\*  
(Temperature in F, heat capacity in Btu lb<sub>m</sub><sup>-1</sup>F<sup>-1</sup>)

Gas	Equation	Range 260 to 1440 F
Air	$c_p = 0.239 + 0.00003t$	
H <sub>2</sub> O	$c_p = 0.434 + 0.000079t + 0.0000000064t^2$	
CO <sub>2</sub>	$c_p = 0.214 + 0.000063t$	
Air	$c_v = 0.170 + 0.00003t$	
H <sub>2</sub> O	$c_v = 0.324 + 0.000079t + 0.0000000064t^2$	
CO <sub>2</sub>	$c_v = 0.169 + 0.000063t$	

\* This table has been constructed from more complete data presented in Table IIA, Appendix.

The precise value for the average or mean heat capacity between two temperatures  $t_1$  and  $t_2$  is

$$c_{avg} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} c_x dt \quad (4-9)$$

The empirical heat-capacity equations listed in Table 4-1 are for temperatures in degrees Fahrenheit. Since many temperature scales

are in common use, the scale used to construct the equation must be known.

**Example 2:** Determine the average heat capacity at constant pressure for air between temperatures of 100 and 500 F (Pressure is 25 psia)

**Solution:** From Table 4-1

$$c_p = 0.239 + 0.00003t$$

From Eq (4-9),

$$\begin{aligned}(c_p)_{\text{avg}} &= \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} c_p dt \\ &= \frac{1}{400} \int_{100}^{500} (0.239 + 0.00003t) dt \\ &= \frac{1}{400} \left[ (0.239t + 0.000015t^2) \right]_{100}^{500} \\ &= 0.248 \text{ Btu/lb}_m \text{ F} \quad \text{Ans}\end{aligned}$$

A visual estimation of the average value of  $c_p$  in Fig 1A (Appendix) for this range is 0.245. The discrepancy lies in the failure of the simple equation of Table 4-1 to correlate the more precise data of Fig 1A. (Note ranges of Table 4-1.)

**4-8 The Irreversible Process<sup>1</sup> and the  $\int p dv$**  For a reversible process of a closed system the  $\int p dv$  is work. For an irreversible process what significance is

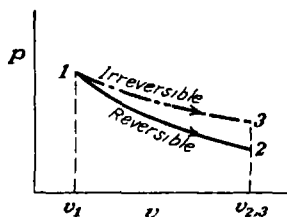


Fig 4-11 Reversible and irreversible adiabatic expansion processes on  $p-v$  diagram

there to this integral? This question can be answered by studying a reversible and an irreversible process that pass through the same series of states. Consider the familiar system of fluid confined in a cylinder by a piston, Fig 4-1 or 4-2, for example. Assume that the fluid expands reversibly and adiabatically from state 1 to state 2 as illustrated in Fig 4-11. Now suppose that an irreversible (but adiabatic) process is to start from state 1. The irreversibility could be friction between piston and cylinder, or the system of Fig 4-2 could be operated in a series of fast expansions, stopping the piston after each short expansion to allow the pressure to equalize between the two chambers. By such means (however impractical) an irreversible path could be determined or approximated. For the irreversible process at any state of the expansion less energy will be removed as work, consequently, more energy will remain in the system than in the reversible case, and the pressure will be *higher*. From this reasoning the path 1-3 for the irreversible process must lie *above* the path for the reversible process 1-2.

The same path 1-3 can be reversibly traveled if heat is added while the expansion is under way, provided, of course, no irreversibilities are present. For the

<sup>1</sup> This article is not a prerequisite for material that is to follow in other chapters

reversible process the First Law shows that

$$\begin{aligned} Q - W_{\text{rev}} &= \Delta U_{1-3} \\ \int_1^3 p dv &= W_{\text{rev}} = -\Delta U_{1-3} + Q \end{aligned} \quad (a)$$

while, for the irreversible adiabatic process,

$$\begin{aligned} Q - W_{\text{irrev}} &= \Delta U_{1-3} \quad \text{and} \quad Q = 0 \\ \text{or} \quad W_{\text{irrev}} &= -\Delta U_{1-3} \end{aligned} \quad (b)$$

Substituting Eq (b) in Eq (a),

$$\int_1^3 p dv = W_{\text{irrev } 1-3} + Q_{\text{rev } 1-3} \quad (c)$$

But no heat was added in the irreversible process, and Eq (c) can better be written

$$\int_1^3 p dv = W_{\text{irrev } 1-3} + F_{1-3} \quad (4-10)^*$$

Comparison of Eqs (4-10) and (c) shows that the term  $F$  is entirely equivalent to a transfer of heat and represents dissipation of available energy in turbulence and friction. This equivalence is not strange because the distinction between heat and work is a matter of definition. If the process 1-3 is reversibly conducted, the  $\int p dv$  is work or energy *removed* from the system, although at the same time energy must be *added* (and this energy is called *heat*). The system, however, is conscious only of the difference in value of the net energy (and is not conscious of man-made distinctions between heat and work). In the irreversible case, less energy was removed as work but no energy was added as heat, and the energy within the system at any stage of the expansion was exactly the same in amount as during the reversible process. The irreversible adiabatic process and the reversible (but not adiabatic) process followed the same path on a diagram of properties although the transfers of heat and work were quite different.

In many instances, comparison is made between an irreversible and a reversible process *even though the state points of the process are not the same*. For example, in Fig 4-11 the reversible path 1-2 is the ideal path that the real expansion process 1-3 attempts (but never is able) to follow. Therefore, the maximum amount of work for either of the adiabatic expansion processes cannot exceed the reversible work for path 1-2. For this reason the  $\int_1^2 p dv$  for the reversible adiabatic path can be used as the criterion of excellence for the real adiabatic process and

$$\int_1^2 p dv = W_{\text{rev } 1-2} = W_{\text{irrev } 1-3} + \text{loss of available energy}$$

Note, however, that the above amount of work ( $W_{\text{rev } 1-2}$ ) does not equal the friction  $F$  plus the irreversible work ( $W_{\text{irrev } 1-3}$ ) because  $F$  is not a complete loss of

\* For the inverse compression process note that the sign of  $\int p dv$  and  $W$  will be minus ( $-$ ) but  $F$  will remain positive ( $+$ ) because, for either direction of the process,  $F$  is available energy dissipated *within* the system as a thermal effect

**available energy** The effect of friction is equivalent to a transfer of heat that would enable the process to do an additional amount of work. This apparent gain (of amount  $\int_1^3 p dv - \int_1^2 p dv$ ) is secured only by dissipating a much greater quantity of available energy (of amount equal to  $F$ ), and, of course, it is entirely probable that no work at all will be done by the irreversible expansion process.

By similar arguments, the work of the irreversible flow process is obtained by superimposing the supplementary forms of energy that accompany flow

$$W_{\text{urev}} + F = \int p dv - \Delta FE - \Delta KE - \Delta PE \quad (4-11a)$$

and

$$W_{\text{irrev}} + F = -\int v dp - \Delta KE - \Delta PE \quad (4-11b)$$

**Example 3:** Textbooks on fluid flow have equations like

$$\int v dp + \Delta KE = W - \Sigma F \quad (a)$$

and, when no work is involved,

$$-v dp = \frac{g}{g_c} dz + \frac{V dV}{g_c} + dF \quad (b)$$

where  $F$  is defined as friction or vaguely as the term necessary to balance the equation when irreversible flow occurs. Discuss.

**Solution:** Equations (a) and (b) may be rearranged and compared with Eq (4-11b)

$$\begin{array}{ll} \text{Eq (4-11b)} & -\int v dp - \Delta KE = W + F \\ \text{Eq (a)} & -\int v dp - \Delta KE = -W + \Sigma F \\ \text{Eq (b)} & -v dp - d(KE) - d(PE) = dF \end{array}$$

Comparison shows that the  $F$  term corresponds to the dissipation of available energy into a heating effect. Note that the signs of  $W$  in Eq (4-11b) and Eq (a) differ. When this difference is encountered, it will be found that  $+W$  is defined as work done on the system, whereas in this text the opposite convention is used.

Equations (4-11) illustrate the limit of the ability of thermodynamics to explain flow friction. If additional information is required on the factors influencing friction, other means must be adopted such as dimensional analysis (Art 1-11)

### Problems

1. A cycle consists of three reversible processes. process A,  $W = 7$  Btu,  $Q = 5$  Btu, process B,  $W = 0$ ,  $Q = -4$  Btu, process C,  $W = -6$  Btu,  $Q = 0$  Btu. Compute the work and thermal efficiency of the cycle.

2. List, to the best of your knowledge, and explain all the possible irreversibilities that may be present in a system.

3. Divide the irreversibilities listed in Prob. 2 into internal and external effects.

4. An air compressor has a cooling-water jacket, and a  $100^\circ$  differential in temperature exists between the air in the cylinder and the cooling water. If the system is the air enclosed in the compressor, can the compression process be considered to be a reversible process? Explain.

5. For a reversible process the increase in total energy is 6 Btu while heat of amount 10 Btu is abstracted. Compute the work and explain the algebraic sign.

6. An irreversible process that passes through the same series of states as the reversible process of Prob. 5 has 12 Btu of heat transferred to the surroundings. Compute the work that can be transferred.

7. A reversible process of a closed system is observed to maintain a relationship  $pv = C$  (constant) between pressure and specific volume during the process. Derive a formula for the work done.

8. Derive a general formula for the work of reversible processes of closed systems if the pressure-specific-volume relationship is  $pv^n = C$  where  $n$  and  $C$  are constants.

9. Repeat Prob. 7, but this time assume an open system and steady flow.

10. Repeat Prob. 8, but this time assume an open system and steady flow.

11. A pound mass of air (at a low pressure) is reversibly heated at constant volume from 32 to 300 F. How much heat must be transferred? Find the average value of the heat capacity.

12. A pound mass of carbon dioxide (at a low pressure) is reversibly heated at constant volume from 100 to 1000 F. Find the heat transferred and mean heat capacity.

13. Repeat Prob. 12, but assume that the fluid is water vapor (steam).

14. In Probs. 11, 12, and 13 each fluid is contained in an iron tank that weighs 20 lb<sub>m</sub>. How much heat must be added to the system of tank and fluid? (Heat capacity of the material of the tank can be found in Table III, Appendix.)

15. A pound mass of air at a temperature of 100 F is heated to 500 F at constant volume by an irreversible process that involves heat and work. Find the internal energy at both states if the datum of zero internal energy is at 0 F and the effect of pressure can be ignored.

16. Repeat Prob. 11 with the process at constant pressure.

17. Repeat Prob. 12 with the process at constant pressure.

18. For the data and conditions of Prob. 15, find the enthalpy at both states if the datum of zero enthalpy is at 0 F. Is the change in enthalpy between the two states equal to the heat added?

19. For the conditions of Prob. 15, assume that the tank is converted to a cylinder and piston and that the pressure remains constant during a reversible process. Compute the change in enthalpy. Is this value equal to the heat added?

20. Find the enthalpy of air at several temperatures from 0 to 1000 F, and plot with  $h$  as the ordinate and temperature as the abscissa. Construct a curve passing through these points and show tangents to the curve at several points. Discuss meaning and values for the change in slope. (Assume that enthalpy of air is unaffected by pressure.)

21. Show that, if the effect of pressure is negligibly small on the heat capacity at constant volume, an isothermal process is a process at constant internal energy.

22. In a reversible, steady-flow process, the specific volume of the fluid remains constant although changes in pressure, enthalpy, internal energy, kinetic energy, and potential energy occur. Show that Eq. (4-5) is valid for this process.

23. Water under a pressure of 100 psia enters a 2-in. pipe at a mass rate of 10 lb<sub>m</sub> sec<sup>-1</sup>. The exit from this system is a 1-in. pipe at an elevation of 30 ft above the inlet, and the water leaves with pressure of 50 psia. If no work is

done by this system, determine the friction in foot pounds force per pound mass of water (Assume water to be incompressible, with density of  $62.3 \text{ lb}_m/\text{ft}^3$ )

**24.** Determine the indicated work in foot pounds force for a reciprocating-piston engine that has a bore (cylinder diameter) of 3 in. and a (piston) stroke of 4 in. (these data are usually abbreviated  $3'' \times 4''$ ) if the area of the indicator diagram is  $1.38 \text{ in}^2$ . The reducing motion that drives the drum of the indicator has a ratio of 2 to 1 and the spring scale is  $100 \text{ psi in}^{-1}$ .

**25** Repeat Prob. 8, but assume that the engine dimensions are 4 by 5 in.

### Symbols

$A$	area
$c$	heat capacity
$C$	constant
$E$	total energy
$F$	friction, turbulence dissipation of work or available energy
$FE$	flow energy
$g$	local acceleration of gravity
$g_c$	dimensional constant
$h$	enthalpy per unit mass (always in thermal units) (specific)
$k$	ratio of $c_p$ to $c_v$
$KE$	kinetic energy
$L$	length
$m$	mass, also, mass rate of flow
$n$	a constant
$PE$	potential energy
$p$	pressure
$Q$	heat
$t$	temperature, any reproducible scale
$U$	internal energy (always in thermal units)
$u$	internal energy per unit mass (always in thermal units) (specific)
$V$	volume, also, velocity
$v$	specific volume
$W$	work
$a < b$	$a$ less than $b$
$a > b$	$a$ greater than $b$

### Subscripts

avg	average	$p$	pressure constant
$f$	force	rev	reversible
irrev	irreversible	$v$	volume constant
$m$	mass	$x$	any process
		0	atmospheric









## CHAPTER V

### THE SECOND LAW

It is impossible to construct an engine which will work in a complete cycle and produce no other effect except the raising of a weight and the cooling of a heat reservoir <sup>1</sup>

**5-1. Limitations of the First Law.** The First Law is a statement of the equivalence of all forms of energy. According to this law, whenever energy in one form disappears, an equal quantity in another guise must appear, and, therefore, the result of any change can be revealed by *examining all the forms of energy involved in the change*. The First Law makes no attempt to designate a system or process that can best be used to effect a change. Whether a system or a process is perfect need not be considered. For real or for ideal systems the First Law is a rigid bookkeeper to ensure that energy is neither created nor destroyed but only changed in form.

One of the primary interests of the engineer is the complete conversion of heat into mechanical work. Nothing in the First Law implies that any difficulty will be encountered in making this conversion, especially since the inverse operation of completely converting work into heat is readily accomplished. A *process* can be devised to produce work of amount equal to the heat added, but *all efforts to form a cycle that will continuously and completely convert heat into work are marked by failure*. This failure is all the more striking in that the best systems yet devised fail by far to approach 100 per cent thermal efficiency. Values of 40 per cent are rare indeed, while thermal efficiencies of 5 and 10 per cent are usual. Since much of man's effort is directed toward the production of work from heat, clearly it is to his interest to investigate thoroughly the limitations that may be present in this conversion.

**5-2. The Second Law.** The Second Law denies the possibility of ever completely converting into work all the heat supplied to a system operating on a cycle no matter how perfectly designed or skillfully made a machine may be. Planck's statement of the Second Law is

<sup>1</sup> PLANCK, MAX "Treatise on Thermodynamics," p. 86, Longmans, Green & Co., Inc., New York, 1903

entirely adequate for engineering thermodynamics, which deals, most generally, with the production of work from other forms of energy.

**It is impossible to construct an engine which will work in a complete cycle and produce no other effect except the raising of a weight and the cooling of a heat reservoir.<sup>1</sup>**

In other words, any system operating on a cycle and receiving heat while doing work must also have a heat-rejection process as part of the cycle

[ The Second Law is not restricted to interchanges of heat and work, but it is rather a broad philosophy on the behavior of energy and energy transformations. Many statements of the Second Law have been proposed; one of the most famous is that of Clausius <sup>2</sup>

**Heat cannot, of itself, pass from a colder to a hotter system.**

Here, the obvious is recognized. Heat cannot flow "uphill", that is, the potential gradient of temperature must be in the direction of the flow of heat. The thought of Clausius can be expanded to include not only temperature but all intensive properties (potentials)

**Energy cannot, of itself, pass from a lower to a higher potential. ]**

When it is realized that the ability of a system to do work is measured by its intensive properties (of temperature and pressure, for example), the inability of the system (unaided by any external agency) to increase its potentials appears reasonable if not self-evident.

A necessary corollary of the above statements is the inevitable degradation of *available energy of the surroundings* that must occur with all real processes because a potential difference is a necessary condition for the transfer of energy. If in a cycle of processes the intensive factors of the system cannot increase (without aid) but can decrease (without aid), then the available energy of the surroundings (which furnish the aid) must be constantly decreasing (although the energy of the surroundings remains constant). In other words, the amount

<sup>1</sup> In earlier articles it has been emphasized that only energy, and not heat, can be stored in a system because heat, by definition, is energy in transit across a system boundary under the driving potential of a temperature difference. But when a system serves as a heat source, it is quite convenient to use the name *heat reservoir* if only to indicate the nature of the energy transfer. A *heat reservoir*, then, is the name given to a system that serves as the *source* for the energy transferred as heat. For isothermal transfer of heat, the reservoir must be infinitely large if the temperature is to remain constant while heat is transferred.

<sup>2</sup> Rudolf Clausius (1821-1888)

of energy in the surroundings that can be converted into work by a system must be constantly decreasing because all real processes are irreversible

The First and Second Laws cannot be proven true; their validity rests upon the fact that all attempts to disprove them have failed. In the following articles will be presented the logic and concepts underlying the Second Law.

**5-3. The Carnot Cycle.** The foundations for the Second Law were laid in 1824 by Sadi Carnot, a young Frenchman, who published an essay entitled "Reflections on the Motive Power of Heat." Carnot pointed out the fact that, whenever a difference of temperature exists, a system can be devised to produce work, and the greater the fall in temperature experienced by the system, the greater will be the amount of work done. Carnot reasoned that temperature alone must be the factor responsible for the ability of heat to do work, and that other properties such as pressure, or any special qualities of the working fluid, were not significant. To illustrate his premise, Carnot invented a cycle that would take in heat at constant temperature, do work, and reject heat at another constant temperature. Figure 5-1 illustrates a Carnot reversible engine cycle that consists of four processes

- ab.* Adiabatic compression to the higher temperature  $t_H$
- bc* Isothermal addition of heat (expansion) at the higher temperature  $t_H$  followed by
- cd* Adiabatic expansion to the lower temperature  $t_L$
- da* Isothermal rejection of heat (compression) at the lower temperature  $t_L$

In Fig 5-1 the working fluid is adiabatically compressed (*ab*) from the lower to the higher temperature. Heat is then added while the fluid isothermally expands (*bc*). At some portion of the stroke the transfer of heat is discontinued and the gas adiabatically expands (*cd*) to the lower temperature. During both of these expansion processes work is done by the system. The cycle is completed by isothermally compressing the gas (*da*) and so rejecting heat to another reservoir (called the *sink*). Both compression processes (*da*) and (*ab*) require work to be done on the system. The net effect of the cycle is that heat is added at one constant temperature and rejected at another constant temperature, with the algebraic sum of these heat quantities being equal to the work done by the cycle.

Carnot checked each process of his cycle for reversibility to ensure that imperfections were absent. When operating on the reversed

cycle the system became a *heat pump* with heat added at the lower temperature and rejected at the higher temperature. Necessarily, work is transferred to the system. The cycle of the heat pump consists of the same reversible processes as for the heat engine but executed in the inverse direction:

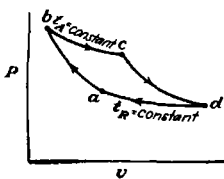
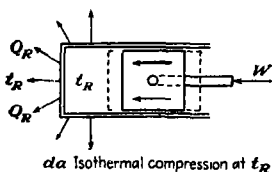
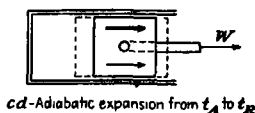
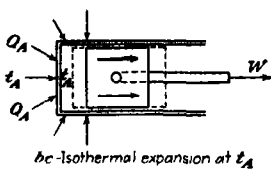
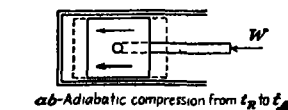


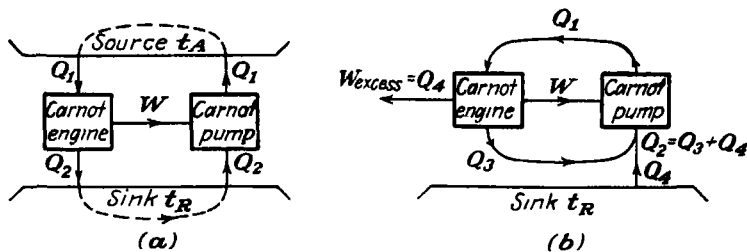
Fig 5-1 The Carnot cycle of processes (as conducted with nonflow processes)

some factor other than temperature could make the Carnot cycle more efficient, for example, a different gas used as the working fluid. Let this more efficient fluid be used only in the heat engine, more work will be delivered by the heat engine than is required to drive the heat pump (Fig 5-2b). A high-temperature reservoir is not necessary because the heat rejected by the heat pump exactly equals the heat input to the engine, and therefore the net effect of the system

- $dc$  Adiabatic compression from the lower temperature to the higher temperature followed by
- $cb$  Isothermal compression with consequent rejection of heat to a high-temperature reservoir
- $ba$  Adiabatic expansion from the higher to the lower temperature followed by
- $ad$  Isothermal expansion with addition of heat from a low-temperature source

After devising a cycle and the concept of reversibility, Carnot was now in a position to demonstrate that neither the working fluid nor any factor other than temperature could affect the thermal efficiency of his ideal engine. To prove this, he set up the system illustrated in Fig 5-2a. A Carnot engine abstracts heat from a source at  $t_A$  and rejects heat to a sink at  $t_R$  while driving a reversed Carnot engine (heat pump). The heat pump receives heat from the low-temperature sink and transfers heat to the high-temperature reservoir. The net effect of this system must be zero because the work output of the heat engine exactly equals the work input to the heat pump. Now let it be supposed that

will be to produce work while obtaining heat from a low-temperature reservoir. This result is so contrary to experience that the premise that a change in working fluid can affect the efficiency of a Carnot cycle must be false.



$$\left[ \eta_t [\text{Carnot engine (a)}] = \frac{W}{Q_1} < \eta_t [\text{Carnot engine (b)}] = \frac{W + W_{\text{excess}}}{Q_1} \right]$$

FIG. 5-2 Carnot engine and heat pump

By pursuing the same line of thought, the following deductions can be made

For definite temperatures of source and sink: No engine can be more efficient than a reversible engine. All reversible engines have the same efficiency. The efficiency of a reversible engine is independent of the working fluid. (This is the case shown in Fig 5-2) A system not receiving work cannot convey heat from the cold to the hot reservoir. (Clausius. Heat cannot, of itself, pass from a colder to a hotter body)

Yet, no conclusions can be made of the comparative efficiencies of Carnot engines operating between different thermal levels. For example, the Carnot engine operating between  $1000^{\circ}$  and  $900^{\circ}$  cannot be compared with a similar engine operating between  $800^{\circ}$  and  $700^{\circ}$  because these thermal levels, in Carnot's day, were arbitrarily established. Such comparison must wait until a thermodynamic temperature scale is defined.

Note that, since the work output of the Carnot engine depends on the temperature of source and sink, the *pressure* exerted by the working fluid is only incidental to the production of work. In engineering, one goal is to use the widest possible range of temperatures between source and sink to obtain high thermal efficiency, another goal is to use pressures sufficiently low to obtain safety and ease of design, but sufficiently high to obtain reasonable size and cost.

**5-4. The Thermodynamic Temperature Scale.** At the time of Carnot the temperature scales in existence were arbitrary scales that

related the hotness, or thermal level, of a body to some particular property of the thermometer. Such thermometers served only as arbitrary indicators of the relative thermal state and, although reproducible, did not define a universal property of temperature (or a fundamental dimension).

In 1848, Lord Kelvin realized that the logic of Carnot opened the way for the definition of a thermodynamic scale of temperature that would be independent of the properties of any particular material. The efficiency of the Carnot cycle depended only upon the temperatures of source and sink and increased as the sink temperature was reduced (or as the source temperature was raised). This concept in itself defined a condition of absolute zero as the lowest possible sink temperature for an engine because no energy would be rejected and all of the energy entering the engine would be converted into work. To develop a temperature scale consider a reversible Carnot engine and let  $t_A$  be the thermal level of the source and  $t_R$  that of the sink. The Carnot premise was

$$\eta_t = f(t_A t_R)$$

But the efficiency of the cycle also is defined by

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{Q_A + Q_R}{Q_A} = f(t_A t_R)$$

This can be written (note that  $Q_R$  is a negative quantity)

$$\eta_t = 1 + \frac{Q_R}{Q_A} = f(t_A t_R)$$

and therefore

$$\frac{Q_R}{Q_A} = f'(t_A t_R) \quad (a)$$

In Carnot's time,  $t_A$  and  $t_R$  were arbitrary numbers related to some property of the thermometer. Although a function could undoubtedly be found to relate these arbitrary temperatures to thermal efficiency, Kelvin suggested that Eq. (a) be used to define a new absolute thermodynamic temperature scale (which would be independent of the properties of the thermometer). He proposed that

$$\frac{-Q_R}{Q_A} = \frac{T_R}{T_A} \quad (5-1a)$$

and therefore the efficiency of the Carnot cycle would be

$$\eta_{t(\text{Carnot})} = \frac{Q_A + Q_R}{Q_A} = \frac{T_A - T_R}{T_A} = 1 - \frac{T_R}{T_A} \quad (5-1b)$$

where  $T_A$  and  $T_R$  would be absolute thermodynamic temperatures. Existing scales could be calibrated in terms of this new absolute scale. For example, the centigrade scale has two fixed<sup>1</sup> points: the *ice point*, arbitrarily called 0 C; and the *steam point*, arbitrarily called 100 C. To determine the absolute thermodynamic temperatures of these fixed and reproducible states in terms of the centigrade degree, a Carnot engine could be used. Assume that a laboratory model engine with air used as the working fluid could approximate the cycle of a Carnot engine. Let 10 Btu of heat be isothermally added at a temperature level of 100 C, as measured with a mercury thermometer, and the amount of heat rejected be measured at a receiver temperature of 0 C, again as measured by a mercury thermometer. Let it be supposed that this rather impractical experiment was carefully performed, and by measurement 7.32 Btu of heat was found to be rejected. Then, since on the absolute scale there exists a point of absolute zero lying an unknown distance  $z$  below the arbitrary 0 C, by Eq. (5-1a),

$$\begin{aligned}\frac{T_R}{T_A} &= \frac{-Q_R}{Q_A} \\ \frac{z + 0^\circ}{z + 100^\circ} &= \frac{7.32}{10} \\ z &= 273^\circ\end{aligned}$$

More practical methods show this figure to be  $273.160 \pm 0.010^\circ$ . The absolute thermodynamic temperatures of the ice and steam points are (to the best of present knowledge),

$$\begin{aligned}\text{Ice point} &= 273.16^\circ \\ \text{Steam point} &= 373.16^\circ\end{aligned}$$

The intermediate points between the ice and steam points have also been determined, as well as other fixed and reproducible states. Thus the temperatures of what was a purely arbitrary scale, the centigrade scale, have been converted to thermodynamic temperatures.

Although the terms *absolute* and *thermodynamic* many times are used synonymously, a more precise meaning can now be assigned. An *absolute* temperature is also a *thermodynamic* temperature and is defined by Eq. (5-1). A *thermodynamic* temperature differs from an absolute temperature only by an additive constant. The centigrade and Fahrenheit scales of today are thermodynamic scales (but not absolute scales) calibrated to be independent of the materials used in constructing the thermometers.

<sup>1</sup> Refer to Art. 1-10



In honor of Kelvin, the absolute thermodynamic scale, with degrees equal to those of the thermodynamic centigrade scale, bears his name and

$$^{\circ}\text{K} = ^{\circ}\text{C} + 273.16^{\circ} \quad (5-2)$$

In succeeding pages, degrees Kelvin will be designated only by the letter K and degrees centigrade by the letter C, as for example

$$100\text{ C} = 373.16\text{ K}$$

The symbol for absolute temperature will be  $T$ , while the lower case letter  $t$  will now refer to any thermodynamic temperature

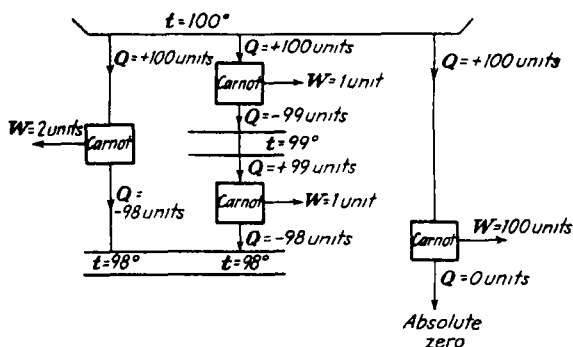


FIG 5-3 A linear absolute temperature scale

In a similar manner the absolute scale with degrees equal to those on the Fahrenheit scale is called Rankine<sup>1</sup> and

$$^{\circ}\text{R} = ^{\circ}\text{F} + 459.69^{\circ} \quad (5-3)$$

An infinite number of absolute scales could have been devised. For example, if 100 units of heat enter a Carnot cycle at a certain thermal level (say, the melting point of sulphur), then this level could be designated to be 100 degrees absolute on a new absolute thermodynamic scale. A degree is specified to be that temperature difference between source and sink that will allow 1 unit of work to be delivered by the Carnot engine. [This statement is true for all absolute scales defined by Eq (5-1)] When the sink temperature becomes absolute zero, all the entering energy will be converted into work. Figure 5-3 illustrates this relationship for the hypothetical temperature scale as well as for the Rankine and the Kelvin scales.

Even so, the effectiveness of each degree drop in temperature becomes greater as the temperature is decreased. In Fig 5-3 the

<sup>1</sup> William Rankine (1820-1872)

thermal efficiency of the engine operating between 100° and 99° absolute is

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{1}{100}$$

while the engine operating between 99° and 98° has the higher thermal efficiency of

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{1}{99}$$

**Example 1** • A Carnot engine operates between a source at 1000 R and a sink at 500 R. Compare the thermal efficiencies obtained by (a) raising the source temperature by 100 R, (b) lowering the sink temperature by 100 R.

**Solution**

$$\text{Efficiency of original engine } \eta_t = 1 - \frac{T_R}{T_A} = 1 - \frac{500}{1000} = 50 \text{ per cent}$$

$$\text{Efficiency of 1100 R source, 500 R sink} = 1 - \frac{500}{1100} = 54.6 \text{ per cent}$$

$$\text{Efficiency of 1000 R source, 400 R sink} = 1 - \frac{400}{1000} = 60 \text{ per cent}$$

Hence, lowering the sink temperature is more effective than raising by an equivalent amount the source temperature. This was first noted by Carnot.

**Example 2** • The gases in a furnace are at a temperature of 2500 R and pass over a boiler containing water at 1000 R which is to be converted into steam while the temperature and pressure remain constant. Show that the irreversible temperature drop of 1500 R will cause a loss in availability. The sink temperature will be that of the atmosphere, 500 R.

**Solution.** a If a Carnot engine received heat at 2500 R,

$$\eta_t = 1 - \frac{T_R}{T_A} = 1 - \frac{500}{2500} = 0.80, \text{ or } 80 \text{ per cent}$$

Assume 1000 Btu of heat for  $Q_A$ , then,

$$W_{rev} = \eta_t Q_A = 0.8(1000) = 800 \text{ Btu}$$

b If the Carnot engine received the same amount of heat (1000 Btu) at a temperature of 1000 R,

$$\eta_t = 1 - \frac{T_R}{T_A} = 1 - \frac{500}{1000} = 0.50, \text{ or } 50 \text{ per cent}$$

and

$$W_{rev} = 0.50(1000) = 500 \text{ Btu}$$

c The difference in work output between the two cycles because of the difference in temperature of the heat added is

$$800 - 500 = 300 \text{ Btu}$$

Although both cycles receive the same amount of heat, one engine can produce 800 Btu of work (and reject 200 Btu to the sink) while the engine receiving heat at a lower temperature can do only 500 Btu of work (while rejecting 500 Btu to the sink).

The gloomy picture in Example 2 of the effect of a temperature difference can be lightened by viewing the practical necessity for the irreversibility. The temperature difference causes an increased rate of heat transfer that allows a much smaller boiler to be used and thereby effects a saving in the initial cost. Since no material is known that can be subjected to temperatures above 1500 F for long periods of time, the temperature difference becomes an absolute necessity. Also, to transfer heat at the highest possible temperature requires an infinite reservoir of heat, while in a furnace the hot gases will decrease in temperature in proportion to the amount of heat transferred. With the above comments in mind the engineer must effect an economical balance between the factor of thermal efficiency, which demands the highest possible temperature for additions of heat, and the practical factors, which demand the irreversibilities for ease of operation.

**Example 3:** An inventor claims that a new heat-engine cycle will develop 50 hp for a heat-addition rate of 30 Btu min<sup>-1</sup>. The highest temperature in the cycle is 3000 R while the lowest is 1000 R. Are his claims possible?

**Solution:** A Carnot cycle for the same temperature range would have a thermal efficiency of

$$\eta_i = 1 - \frac{T_R}{T_A} = 1 - \frac{1000}{3000} = 0.66, \text{ or } 66\frac{2}{3} \text{ per cent}$$

The inventor claims that

$$\eta_i = \frac{\Sigma W}{Q_A} = \frac{50 \text{ hp } (33,000 \text{ ft lb}_f/\text{hp min})}{(778 \text{ ft lb}_f/\text{Btu})(30 \text{ Btu/min})} = 0.707 = 70.7 \text{ per cent}$$

The inventor's claims must therefore be false. The discrepancy is even greater than the figures reveal because all actual engines will have irreversibilities that will prevent close approach to the thermal efficiency of the Carnot. Any claims to thermal efficiencies of over 40 per cent should be viewed with caution.

Lord Kelvin had originally proposed an absolute scale defined as follows

$$\frac{-Q_R}{Q_A} = \frac{\ln^{-1} T_R}{\ln^{-1} T_A}$$

Equating this definition to the linear relationship (so called) gives

$$\frac{\ln^{-1} T_R}{\ln^{-1} T_{A'}} = \frac{T_R}{T_A}$$

$$T_{A'} - T_{R'} = \ln T_A - \ln T_R$$

For the interval  $T_A = 1$ ,  $T_R = 0$ ,

$$T_{A'} - T_{R'} = \infty$$

For the interval  $T_A = \infty$  (an abstract possibility),  $T_R = 1$ ,

$$T_{A'} - T_{R'} = \infty$$

This scale emphasizes the remoteness not only of infinite temperatures but also of absolute zero. It is believed that absolute zero has been experimentally approached to within  $0.001^\circ$ . At the other extreme, a few thousand degrees represent the highest temperature reached by man although temperatures many times this are believed to be reached on the stars. The logarithmic scale illustrates well that  $0.001^\circ$  above absolute zero is as far from the lower limit as several thousand degrees is from an upper limit.

Today, after much experimentation, a thermodynamic scale linking known reproducible states has been evolved. The chief standardization laboratories of the world have agreed upon an international scale that the thermodynamic scale approximates (to the best of laboratory technique). It is based upon the centigrade temperatures shown in Table 5-1.

TABLE 5-1—THE INTERNATIONAL TEMPERATURES OF CERTAIN REPRODUCIBLE STATES\*

Primary Standards	Centigrade
Boiling point of oxygen	-182.97†
Ice point (by definition)	0.000
Steam point (by definition)	100.000
Boiling point of sulphur	444.60
Freezing point of silver	960.5
Freezing point of gold	1063
Secondary Standards	
Freezing point of mercury	-38.87
Freezing point of tin	231.85
Freezing point of lead	327.3
Freezing point of zinc	419.4
Freezing point of aluminum	660.1
Melting point of platinum	1773
Melting point of tungsten	3400

\* BURGESS, G. K. The International Temperature Scale, *Bur. Standards J. Research*, **1**, 635 (1928).

† The last decimal point given for each of the above values is significant only as regards reproducibility of that fixed point, and the point is not necessarily known on the thermodynamic scale to the corresponding degree of accuracy.

For interpolation between these fixed points, international agreement has standardized various methods and indicators as being the best available at this date. One of these means is the platinum resistance thermometer for measuring temperatures between the ice point and  $660^\circ\text{C}$ . The temperature is related to the resistance of platinum by the formula

$$R_t = R_0(1 - At - Bt^2)$$

The constants  $R_0$ ,  $A$ , and  $B$  of this formula are determined by calibration at the ice, steam, and sulphur points.

**5-5. Definition of Entropy.** As a necessarily first consequence of the Carnot cycle, a relationship was found,

$$\frac{T_R}{T_A} = \frac{-Q_R}{Q_A}$$

that defined a thermodynamic temperature scale (The minus sign is inserted because  $Q_R$  is a negative number) Clausius noted that this relationship could be rearranged to show that

$$\frac{-Q_R}{T_R} = \frac{Q_A}{T_A} \quad \text{and} \quad \frac{Q_A}{T_A} + \frac{Q_R}{T_R} = 0$$

Or, for the Carnot cycle, the cyclic change in the quantity  $Q/T$  is zero. But whenever a cycle occurs and the system returns to its initial state, the net change in a property is zero. Then,  $Q/T$  must be a property, at least for any system employing the Carnot cycle. It can be proved (Art 5-3) that all reversible cycles operating between definite and isothermal source and sink temperatures must have the same thermal efficiency as a Carnot cycle operating between the same temperatures.

$$\eta_{t(\text{rev})} = 1 - \frac{T_R}{T_A} = 1 + \frac{Q_R}{Q_A}$$

Thus, it would appear that  $Q/T$  is a property not only of the Carnot cycle but of any reversible cycle. Also, it will be shown that, if heat is added and rejected at variable instead of constant temperatures, such an arrangement can always be replaced by an infinite number of Carnot cycles. For each reversible process of the reversible cycle the change in  $Q/T$  can be calculated from

$$dS = \frac{dQ}{T} \Big]_{\text{rev}} \quad (5-4)$$

The property represented by the letter  $S$  is called *entropy*, and Eq (5-4) is the defining equation for entropy. Whenever heat is *added* to the system, the entropy *increases*, when heat is *reversibly taken away*, the entropy *decreases*. The units for entropy are

$$\Delta S = \text{Btu/R}$$

and for unit mass (the usual units in this text)

$$\Delta s = \text{Btu/lb}_m \text{ R}$$

Equation (5-4) can be used to find the absolute entropy of a substance at a particular state by calculations based on a reversible path from absolute zero (Art 11-16). Still, the uncertainty in the experimental data for the changes that occur in the substance at the lower temperatures makes it easier to follow the same procedure as was followed for internal and potential energy. This, simply, is to define a

datum state of zero entropy (or zero internal energy or zero potential energy) and to calculate the entropy (or internal or potential energy) at any other state

Why define a new property? And especially an abstract mathematical relationship that cannot be directly observed? One simple answer to these questions is found in the singular fact that heat has only one measurable property, temperature. It has already been noted that heat and work are alike by definition and, more important, in effect. But work can be measured as a function of two properties. Compression work (which is the particular form studied by the mechanical engineer) is measured by

$$W_{\text{rev}} = \int p dv$$

nonflow

Equation (5-4) establishes two properties for the measurement of heat—an intensive or potential property, temperature, and an extensive property, entropy

$$Q_{\text{rev}} = \int T dS = m \int T ds \quad (5-5)$$

The utility for this property will be illustrated in the following sections

**5-6. Entropy and the Carnot Cycle.** Consider a Carnot cycle with heat supplied at 1000 R and rejected at 500 R. If 100 Btu of heat are supplied (per unit mass of fluid) to this system, what changes occur during each process? For these conditions

$$\eta_t = 1 - \frac{T_R}{T_A} = 1 - \frac{500}{1000} = 0.50$$

then

$$W = \eta_t Q_A = 50 \text{ Btu/lb}_m$$

and

$$Q_R = -(Q_A - W) = -50 \text{ Btu/lb}_m$$

Process *ab* Reversible and adiabatic compression from  $T_R$  to  $T_A$

$$\Delta s_{ab} = 0 \quad (Q = 0)$$

Process *bc* Reversible addition of heat at constant temperature  $T_A$

$$\Delta s_{bc} = \frac{Q_A}{T_A} = \frac{100}{1000} = 0.1 \text{ Btu/lb}_m \text{ R}$$

Process *cd* Reversible and adiabatic expansion from  $T_A$  to  $T_R$

$$\Delta s_{cd} = 0 \quad (Q = 0)$$

Process *da* Reversible rejection of heat at constant temperature  $T_R$

$$\Delta s_{da} = \frac{Q_R}{T_R} = \frac{-50}{500} = -0.1 \frac{\text{Btu}}{\text{lb}_m \text{ R}}$$

$$\sum \left[ \frac{Q}{T} \right]_{\text{rev}} = \sum \Delta s = 0$$

The total change of  $Q/T$  in this cycle of reversible changes is zero, as was to be expected

Since entropy is a property, a datum can be arbitrarily selected. For this problem the state at point  $a$  (as defined by the pressure, temperature, and volume) will be assigned a value of zero entropy, then,

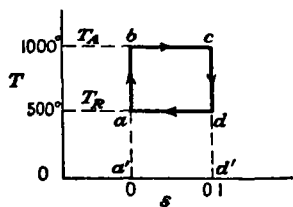


FIG 5-4 Temperature entropy diagram for the Carnot cycle

State	Temperature, R	Entropy
a	500	0
b	1000	0
c	1000	0.1
d	500	0.1

In Fig 5-4 these data are shown on a diagram of properties named the  $Ts$  diagram. From Eq (5-5) it is apparent that areas on this diagram represent reversible transfers of heat (for unit mass of fluid)

$$\begin{aligned}
 Q_A &= \text{heat reversibly added} = \text{area } a'bcd' \\
 Q_R &= \text{heat reversibly rejected} = \text{area } a'dd' \\
 \hline
 Q_A + Q_R &= \text{work done} = \text{area } abcd
 \end{aligned}$$

THROUGHOUT THIS TEXT ALL  $Ts$  DIAGRAMS ARE DRAWN FOR UNIT MASS OF FLUID

The Carnot cycle has two reversible and adiabatic processes, for these processes entropy is constant

**An isentropic process is defined as a reversible and adiabatic process.**

The conclusion of this article is that Eq (5-4) satisfied the condition of the Carnot cycle that

$$\sum \left[ \frac{Q}{T} \right]_{\text{rev}} = 0$$

**5-7. Entropy and the Reversible Cycle.** Equation (5-4) is not restricted to isothermal additions of heat. A reversible cycle employing a piston and cylinder will be constructed having additions of heat at constant volume and constant temperature, while rejection of heat will be at constant pressure. If the additions and rejection of heat are to be reversible, an infinite number of heat reservoirs, each at a different temperature, will be theoretically required. This annoying technicality can be avoided by noting that an irreversible temperature

difference between system and heat reservoir is an external irreversibility that can be ignored by locating the boundary in a manner such that the irreversibility is in the surroundings (Art 4-3). With this expedient an internally reversible cycle can be theoretically devised for any mode of heat transfer.

When heat is added at constant volume, the defining equation is (Art 4-7)

$$dQ_{\text{rev}}]_{v-C} = mc_v dT$$

When this expression is substituted in Eq (5-4),

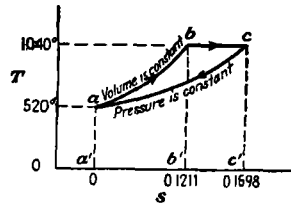
$$dS = \frac{mc_v dT}{T}$$

For simplicity, assume that  $c_v$  is constant (and therefore independent of both temperature and pressure), then, for unit mass,

$$s_b - s_a = c_v \int \frac{dT}{T} = c_v \ln \frac{T_b}{T_a} \quad (5-6)$$

Similarly, for constant-pressure additions of heat,

$$s_c - s_a = c_p \ln \frac{T_c}{T_a} \quad (5-7)$$



A state defined by values for pressure and temperature can be selected and assigned a datum value of zero entropy. For air as the fluid the datum state will be arbitrarily defined by

$$s_a = 0 \quad T_a = 520 \text{ R} \quad p_a = 14.7 \text{ psi}$$

This is state  $a$  on Fig 5-5. A path at constant volume can be constructed from point  $a$  to point  $b$  by assigning small increments to  $T_b$  in Eq (5-6), while the value for  $c_v$  is selected from Table VI (Appendix). Assuming that this is done to trace out the path, the entropy at point  $b$  is found to be

$$\begin{aligned} s_b - 0 &= c_v \ln \frac{T_b}{T_a} & T_b &= 1040 \text{ R} \\ s_b &= 0.175 \ln 2 & c_v &= 0.175 \text{ Btu/lb}_m \text{ R} \\ s_b &= 0.1211 \text{ Btu/lb}_m \text{ R} \end{aligned}$$

and the heat transferred equals

$$\begin{aligned} Q_{ab}]_{\text{rev}} &= c_v(T_b - T_a) \\ &= 0.175(520) \\ &= 91 \text{ Btu/lb}_m \end{aligned}$$

In a similar manner, a path at constant pressure can be traced by assigning small increments to  $T_c$  in Eq (5-7). The entropy at point  $c$  is

$$\begin{aligned} s_c - 0 &= c_p \ln \frac{T_c}{T_a} & T_c &= 1040 \text{ R} \\ s_c &= 0.245 \ln 2 & c_p &= 0.245 \text{ Btu/lb}_m \text{ R} \\ &= 0.1698 \text{ Btu/lb}_m \text{ R} \end{aligned}$$



and the heat transferred equals

$$\begin{aligned} Q_{ac}|_{\text{rev}} &= c_p(T_c - T_a) \\ &= 0.245(520) \\ &= 127.2 \text{ Btu/lb}_m \end{aligned}$$

The work done during a constant-pressure change is

$$-W = -Q + \Delta u$$

and, by Art 4-7,

$$\Delta u = c_v(T_c - T_a) = 91 \text{ Btu/lb}_m \quad (\text{from above})$$

For the reversible process,

$$\begin{aligned} -W_{ac}|_{\text{rev}} &= -127.2 + 91 \\ W_{ac}|_{\text{rev}} &= 36.2 \text{ Btu/lb}_m \end{aligned}$$

Since  $c_p$  is larger than  $c_v$ , then for the same temperature difference  $\Delta s$  is greater for the constant-pressure process than for the constant-volume process. This means that the constant-volume path will be steeper than the constant-pressure path on the  $Ts$  diagram.

To complete the reversible cycle an isothermal can be drawn connecting points  $b$  and  $c$ . The heat and work transferred for this process are equal because the internal energy remains constant during this constant-temperature change (Art 4-7, and Prob 21, page 104)

$$Q - W = \Delta u = 0$$

and

$$W_{bc} = Q_{bc} = T(s_c - s_b) = 1040(0.0487) = 50.7 \text{ Btu}$$

With these processes, a reversible cycle can be constructed. For this reversible cycle the change in  $\Sigma Q/T|_{\text{rev}}$  is zero and, to scale (Fig 5-5),

Path	Process	$\Delta s$	$Q_{\text{rev}}$	$W_{\text{rev}}$
$ab$	Constant-volume addition of heat	+0.1211	+ 91	0
$bc$	Isothermal expansion (addition of heat)	+0.0487	+ 50.7	+50.7
$ca$	Constant-pressure (rejection of heat)	-0.1698	-127.2	-36.2
		0	+ 14.5 Btu	+14.5 Btu

$$\begin{aligned} \sum \frac{Q}{T}|_{\text{rev}} &= \sum \Delta s = 0 \\ \text{Area } a'abcc' &= \text{heat added} = Q_A = Q_{ab} + Q_{bc} \\ \text{Area } a'acc' &= \text{heat rejected} = Q_R = Q_{ca} \\ \text{Area } abc &= Q_A + Q_R = \Sigma Q = \text{work done} = \Sigma W \end{aligned}$$

Note that, when heat is added to a process, the entropy increases, while, when heat is rejected, the entropy decreases.

Since the concept of entropy evolved from the Carnot cycle, what is the relationship between a reversible cycle and the Carnot cycle? In Fig. 5-6 each area of width  $\Delta s$  is equivalent to a Carnot cycle. Then, the work or heat transferred from a reversible cycle can be approximately found by summation of all of these small Carnot cycles. By making  $\Delta s$  small, the error becomes less until in the limit,<sup>1</sup> the reversible cycle is exactly equal to an infinite number of Carnot cycles. Then, for any reversible cycle,

$$\sum \left[ \frac{Q}{T} \right]_{\text{rev}} = \sum \Delta s = 0$$

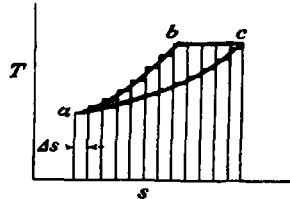


FIG 5-6 Reversible cycle equivalent to summation of Carnot cycles

**Example 4:** Compute the thermal efficiency for the cycle described in this article

**Solution:** The data for the problem are given in the table

Path	Process	Heat	Work
ab	Constant-volume addition of heat	+ 91 0	0
bc	Isothermal addition of heat	+ 50 7	+50 7
ca	Constant-pressure rejection of heat	-127 2	-36 2
		+ 14 5 Btu/lb <sub>m</sub>	+14 5 Btu/lb <sub>m</sub>

The thermal efficiency equals

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{14.5}{141.7} = 0.1022, \text{ or } 10.22 \text{ per cent} \quad \text{Ans}$$

Note that a Carnot cycle operating between the maximum and minimum temperatures of this cycle would have a thermal efficiency of

$$\eta_t(\text{Carnot}) = 1 - \frac{T_R}{T_A} = 1 - \frac{520}{1040} = 0.50, \text{ or } 50 \text{ per cent}$$

The quantity of heat added in the problem was

$$91.0 + 50.7 = 141.7 \text{ Btu/lb}_m$$

If this amount of heat could be reversibly added to a Carnot cycle (and this reversibility may not be possible), the work done would be

$$W_{\text{Carnot}} = \eta_t Q_A = 0.50(141.7) = 70.8 \text{ Btu/lb}_m$$

<sup>1</sup> This is true from the integral calculus, refer to the topic "The Definite Integral as the Limit of a Sum" in any elementary text on the calculus

The results of Example 4 illustrate again the Carnot maxim: *Heat should be added at the highest possible temperature and rejected at the lowest possible temperature if the greatest amount of work is to be gained*

**5-8. The Availability<sup>1</sup> of Heat.** The concept of a perfect heat-engine cycle allows an evaluation to be made of the *availability* of heat. Consider that, whenever a cycle occurs, the system is inevitably restored to its initial state and therefore the work of the cycle is obtained entirely from transformation of heat from a heat reservoir.<sup>2</sup> Now when heat is reversibly transferred to a Carnot cycle, the maximum amount of work is produced when the heat-rejection process of the cycle is made at the same potential as that of the atmosphere ( $T_0$ ). Heat rejected at this temperature is entirely unavailable for

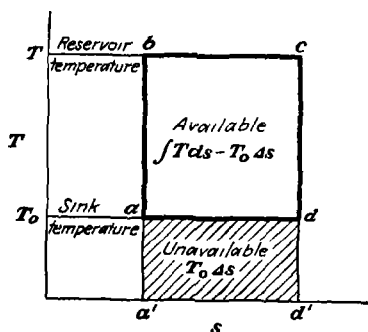


FIG 5-7 Availability of heat from an infinite reservoir

producing work. Consequently, the work done by such a Carnot cycle is also the available part, the *availability*, of the entire quantity of heat abstracted from the reservoir. Thus, the term *availability*, when applied to a quantity of heat, denotes the portion of the heat that could be transformed into work by a Carnot cycle that has its heat-rejection process at the same potential as that of the atmosphere. With this definition of availability, a certain portion of the heat is inherently unavailable energy because even the Carnot cycle will be unable to convert this energy into work.

By definition, then, the *availability*  $\alpha$  of heat transferred at a temperature  $T$  is

$$\alpha \Big|_{T-c} = \left( \frac{T - T_0}{T} \right) Q \quad (5-8a)$$

The maximum work that can be obtained from conversion of heat, the availability, is seen from Eq (5-8a) to be made up of two parts

$$\alpha \Big|_{T-c} = Q - \frac{T_0}{T} Q \quad (5-8b)$$

The first part,  $Q$ , is the total heat transferred, and the second part,  $T_0 Q/T$ , is the portion that is entirely unavailable for the production

<sup>1</sup> A more general definition of availability is given in Art 12-13

<sup>2</sup> See footnote, page 110

of work If the transfer of heat is reversible,  $Q_{rev}/T$  is the change in entropy for the system

$$Q_{rev} \Big|_{T=C} = Q_{rev} - T_0 \Delta s = T \Delta s - T_0 \Delta s = (T - T_0) \Delta s \quad (5-8c)$$

Here

$$Q_{rev} = \text{heat transferred} = T \Delta s \text{ (area } a'bcd', \text{ Fig 5-7)}$$

$$T_0 \frac{Q_{rev}}{T} = \text{unavailable portion} = T_0 \Delta s \text{ (area } a'add', \text{ Fig 5-7)}$$

$$Q_{rev} - T_0 \frac{Q_{rev}}{T} = \text{availability} = T \Delta s - T_0 \Delta s \text{ (area } abcd, \text{ Fig 5-7)}$$

(Whenever the availability of heat is evaluated by properties of the system, reversibility should be specified )

However, most sources of heat are finite rather than infinite, and heat will not be transferred at constant temperature The most efficient way to produce work from this heat would be to use an infinite number of Carnot cycles, each receiving heat at a certain temperature level and all rejecting heat at the temperature of the atmosphere  $T_0$  Equation (5-8b) shows that the maximum work, the availability, will equal

$$a = \sum_{T_1 \text{ to } T_2} \left( Q - \frac{T_0}{T} Q \right)$$

In Fig 5-8, a reversible transfer of heat from a finite source is illustrated The heat transferred equals (area  $a'bcd'$ , Fig 5-8)

$$\sum Q_{rev} = \int_{T_1}^{T_2} T ds$$

The unavailable portion of the heat transferred is (area  $a'add'$ , Fig 5-8)

$$\sum \frac{T_0}{T} Q_{rev} = T_0 \int \frac{dQ_{rev}}{T} = T_0 \Delta s$$

and therefore the availability is equal to

$$\begin{aligned} Q_{rev} &= Q_{rev} - T_0 \Delta s \\ (\text{Area } abcd) &= (\text{area } a'bcd') - (\text{area } a'add') \end{aligned} \quad (5-8c)$$

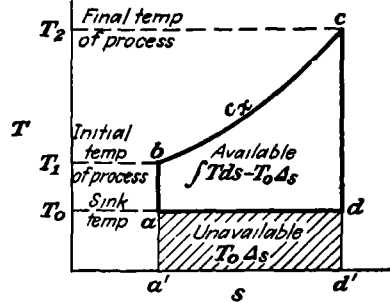


FIG 5-8 Availability of heat from a finite reservoir

Equation (5-8c) can be changed into other forms by noting that

$$Q_{\text{rev}} = \int_{T_1}^{T_2} c_x dT \quad (4-5)$$

Therefore,

$$Q_{\text{rev}} = \int_{T_1}^{T_2} c_x dT - T_0 \Delta s \quad (5-8d)$$

and for a constant-pressure process

$$Q_{\text{rev}} \Big|_{p=c} = \int_{T_1}^{T_2} c_p dT = \Delta h \quad (4-4)$$

Therefore,

$$Q_{\text{rev}} \Big|_{p=c} = \Delta h - T_0 \Delta s \quad (5-8e)$$

The concept of availability is a means for measuring the change in available energy of a system. A system contains energy in many forms; when work is reversibly done by the system, the available energy is decreased by the amount of work reversibly transferred to the surroundings. When heat is reversibly added or taken away from the system, the available energy in the system must also change by an amount equal to the availability of the heat transfer.

$$Q_{\text{rev}} = \text{increase (or decrease) in available} = Q_{\text{rev}} - T_0 \Delta s \quad (5-9a)$$

$$\begin{array}{l} \text{energy of the system from} \\ \text{transfer of heat} \end{array} = \int_{T_1}^{T_2} c_x dT - T_0 \Delta s \quad (5-9b)$$

Then, the net change in available energy of any system between two states can be evaluated by measuring the sum of the reversible amounts of work and availability that can be transferred to (or from) the surroundings during the change of state.<sup>1</sup>

Note that the availability of heat is influenced by the value of  $T_0$  and this value is not a constant because the temperature of the earth and its atmosphere will vary from hour to hour and from season to season. Thus, in winter the real power plant is aided by the low-temperature water that can be circulated through the condenser and the work output is increased (even though low-temperature air must be heated through a greater temperature range).

<sup>1</sup> Although an infinite number of paths can be found between the two states, it matters not what path is selected for evaluating the change in available energy. This statement must be true, for if two paths exist such that each path requires a different sum of work and availability to be furnished, then these two paths could constitute a cycle. The net effect of this cycle would be to transform unavailable energy into available energy. This transformation is denied by the Second Law.

**Example 5:** The hot gases of combustion are produced in a furnace by burning fuel in air at atmospheric pressure, and a maximum temperature of 3000 F is attained. Whether or not the combustion process is efficiently conducted, the hot gases obtained from the process are the finite heat reservoir for a thermodynamic cycle. Determine the maximum thermal efficiency that can be theoretically attained by a cycle using this heat reservoir. (Assume the heat capacity at constant pressure of the gases to be  $0.25 \text{ Btu lb}^{-1} \text{ R}^{-1}$  while the atmospheric temperature is 60 F.)

**Solution:** The maximum amount of heat that can be transferred (area  $a'bcd'$ , Fig. 5-8) is

$$Q_{\text{rev}}]_{p=c} = \int_{3460}^{520} c_p dT = 0.25(520 - 3460) = -735 \text{ Btu/lb}_m \text{ gas}$$

The change in entropy for the reservoir during the heat-transfer process is

$$\Delta s = \int_{3460}^{520} \frac{dQ_{\text{rev}}}{T} = c_p \ln \frac{520}{3460} = -0.475 \text{ Btu/lb}_m \text{ R}$$

When these values are substituted in Eq. (5-8d),

$$\begin{aligned} Q_{\text{rev}}]_{p=c} &= \int c_p dT - T_0 \Delta s \\ (\text{Area } abcd) &= (\text{area } a'bcd') - (\text{area } a'add') \quad (\text{Fig. 5-8}) \\ Q_{\text{rev}}]_{p=c} &= -735 - 520(-0.475) \\ &= -735 + 246 \\ &= -489 \text{ Btu/lb}_m \text{ gas} \end{aligned}$$

(The minus sign merely shows, by convention, that the available energy of the heat reservoir has been decreased.) Thus, the work that can be obtained from an infinite number of Carnot cycles receiving heat of amount 735 Btu is 489 Btu. The unavailable part is 246 Btu. The maximum possible thermal efficiency that can be attained by a system receiving this heat is

$$\eta_c = \frac{Q}{Q_A} = \frac{489}{735} = 0.665, \text{ or } 66.5 \text{ per cent} \quad \text{Ans}$$

If a higher efficiency than this is to be realized, a more efficient heat reservoir must be found, the combustion of the fuel must be improved or some method other than combustion used to release the energy contained in the fuel.

**Example 6:** Devise a practical system that could best use the heat from a finite reservoir.

**Solution:** Here the problem is to replace the infinite number of Carnot cycles with one cycle. Assume that the heat reservoir is a flow stream of hot fluid (for example, gases from the combustion of coal). This heat reservoir could be reversibly cooled while the fluid for the cycle was reversibly heated by using a *counterflow* heat exchanger and a steady-flow process. Either the fluids can be identical in properties, or else the product of mass flow and heat capacity for both streams must be identical to ensure that the rise in temperature of one stream can be exactly compensated by the fall in temperature of the other stream at each section throughout the exchanger. Inspection of Fig. A shows that the cycle fluid could be reversibly heated because the temperature differential between the

two fluids could be imagined to approach zero (although an infinitely long passage would be necessary to heat the cold fluid to  $T$  and cool the hot fluid to  $T_0$ ). The fluid leaving the heat exchanger can be led to a turbine, and, after the turbine, to an isothermal compressor (Fig. B). Although complete reversibility of this system (or any system) is not attained, still, the system appears to be a more practical solution than an attempt to use an infinite number of Carnot cycles



FIG. A Counterflow heat exchanger

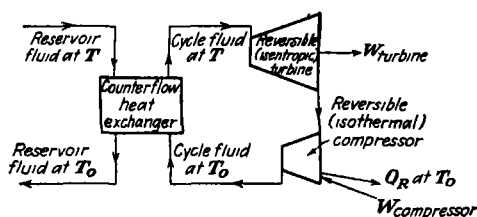
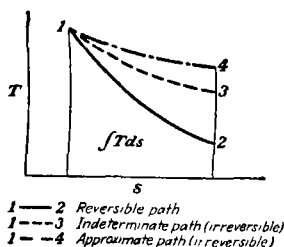


FIG. B Reversible cycle

**5-9. Entropy—a Property of the State.** The entropy of a fluid at any state can be calculated on the basis of heat and temperature measurements made during a reversibly conducted process. Tables of properties are available for fluids representing the relationships between these properties, Fig. II and III (Appendix) are  $Ts$  diagrams constructed from such data. Any point on a property diagram is an equilibrium state. After the diagram (or a Table such as Table V, Appendix) has been constructed, any process can be shown that passes from one equilibrium state to another. The change in entropy for an irreversible process can be found by locating the end states on the property diagram (or by using the table). However, the change of entropy for the irreversible process cannot be calculated from heat and work transfers for the process.

FIG. 5-9 Reversible and irreversible processes on the  $Ts$  diagram

The same restrictions must be made for the  $Ts$  diagram as were made for the  $pv$  diagram (Art. 4-4). A continuous path (1-2 in Fig. 5-9) can be rigorously<sup>1</sup> interpreted only as an internally reversible

<sup>1</sup> Although real processes that approach reversibility will be shown as solid lines in subsequent figures

process. For highly irreversible processes, a dashed line (1-3) will be used to indicate the uncertainty in the states that were encountered because of nonuniform potential gradients. When the irreversible process can be stopped at frequent intervals and an equilibrium state attained, the path could be approximated by connecting together the known equilibrium states (1-4). It is well to repeat that, although irreversible processes can be shown on the  $Ts$  diagram, the entropy of the fluid at each state must have been previously computed for processes that were reversibly conducted. For reversible processes the change in entropy equals  $\Sigma Q/T|_{\text{rev}}$  while for the irreversible process  $\Delta s \neq \Sigma Q/T$ .

**5-10. Entropy and the Irreversible Process.** Since both reversible and irreversible processes can be shown on the  $Ts$  diagram, it should prove instructive to examine and compare these processes. Figure 5-10 represents a temperature-entropy diagram for 1 lb<sub>m</sub> of fluid such as air. If air is isentropically compressed by a piston in a cylinder, the process is represented by  $ab$  on Fig. 5-10. For this process

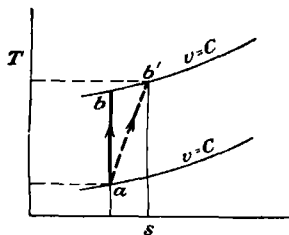


FIG. 5-10 Comparison of reversible and irreversible adiabatic compression processes

$$\Delta s_{ab} = 0 \quad \text{and} \quad \int \frac{dQ}{T} \Big|_{\text{rev}} = 0 \quad \text{because } Q = 0$$

An irreversible but adiabatic compression will require a greater quantity of work to be added to the system for the same volume change as  $ab$ . Therefore, the internal energy at the end of the process will be greater than that corresponding to state  $b$ . The end point will lie on the same constant-volume line as does  $b$  but at a higher temperature because of the greater internal energy. Since this temperature can be measured, point  $b'$  can be located on Fig. 5-10 on the intersection of the known volume and temperature line. The entropy of  $b'$  is greater than that of state  $b$ . For this process

$$\Delta s_{ab'} > 0 \quad \text{and} \quad \int \frac{dQ}{T} = 0 \quad \text{because } Q = 0$$

If process  $ab'$  is reversibly followed, heat must be added during the compression and

$$\Delta s_{ab'} = \int \frac{dQ}{T} \Big|_{\text{rev}}$$



Suppose that the inverse process of expansion is examined. An isentropic expansion is pictured by path  $cd$  in Fig 5-11. For this process

$$\Delta s_{cd} = 0 \quad \text{and} \quad \int \frac{dQ}{T} \Big|_{\text{rev}} = 0 \quad (Q = 0)$$

If the expansion process is adiabatic but irreversible, less work is obtained from the process, and therefore more internal energy remains in the system than for an isentropic expansion. For this reason, the temperature at the end of the irreversible process will be higher than after the reversible process. The end state must lie on the same constant-volume line as does  $d$  but at a higher temperature. From Fig 5-11,  $d'$  must have a greater entropy than  $d$ . For this process

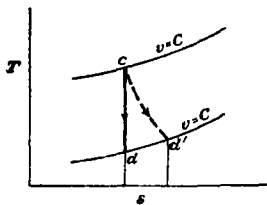


FIG 5-11 Comparison of reversible and irreversible adiabatic expansion processes

$$\Delta s_{cd'} > 0 \quad \text{and} \quad \int \frac{dQ}{T} \Big|_{\text{irrev}} = 0 \quad (Q = 0)$$

Process  $cd'$  can be reversibly followed if heat is added during the expansion and

$$\Delta s_{cd'} = \int \frac{dQ}{T} \Big|_{\text{rev}}$$

Comparison of all of these equations shows that, for the reversible processes,

$$\Delta s = \int \frac{dQ}{T} \Big|_{\text{rev}}$$

while for the irreversible process of either compression or expansion,

$$\Delta s > \int \frac{dQ}{T} \quad (5-10a)$$

A little thought reveals that Eq (5-10a) must be true for all irreversible processes. *Whenever an irreversible process occurs, available energy is dissipated to produce a thermal effect.* The fluid cannot distinguish between energy transferred to the system as heat and energy dissipated within the system to produce the same effect.

**Example 7:** Water in a constant-pressure container is agitated by a paddle until the temperature rises from 60 to 100 F. Compute the change in entropy.

**Solution :** To repeat Eq (5-4),

$$dS = \frac{dQ}{T} \Big]_{\text{rev}}$$

In this case  $Q$  is zero, while the process is irreversible. But entropy is a property of the state, and any path may be selected to pass from the known initial state to the known final state. The specific heat of water is closely  $1 \text{ Btu lb}_m^{-1} \text{ F}^{-1}$  (Table III, Appendix), and

$$\begin{aligned} \Delta S &= \int \frac{mc_p dT}{T} \\ &= mc_p \ln \frac{T_2}{T_1} = mc_p \ln \frac{560}{520} \end{aligned} \quad (5-7)$$

and for  $1 \text{ lb}_m$  of water

$$\Delta s = 0.075 \text{ Btu/lb}_m \text{ R} \quad \text{Ans.}$$

As a more general picture of the effect of irreversibilities, consider the reversible and irreversible cycles illustrated in Fig 5-12. Cycle  $abcd'$  is similar to the Carnot cycle  $abcd$  except that the adiabatic expansion  $cd'$  is irreversible. Both cycles receive the same amount of heat ( $gbcf$ ) from the source at  $T_A$  but the irreversible cycle must reject more heat ( $gad'e$ ) to the sink at  $T_R$  than the reversible cycle ( $gadf$ ). This is a consequence of the irreversibility.

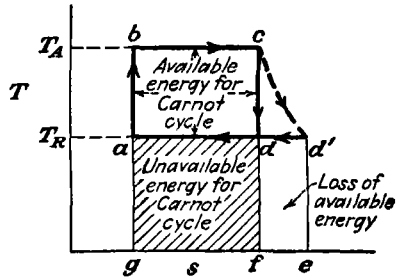


FIG 5-12 Comparison of reversible and irreversible cycles

Figure 5-12 can be considered to be a graphical proof to show that an irreversibility will cause an increase in entropy, while for an analytical proof consider

$$\begin{aligned} &\text{Irreversible} \\ \eta_{t(\text{irrev})} &= 1 + \frac{Q'_R}{Q_A} < 1 - \frac{T_R}{T_A} \end{aligned}$$

and

$$\frac{-Q'_R}{Q_A} > \frac{T_R}{T_A}$$

Therefore,

$$\frac{Q_A}{T_A} < \frac{-Q'_R}{T_R}$$

$$\begin{aligned} &\text{Reversible} \\ \eta_{t(\text{rev})} &= 1 + \frac{Q_R}{Q_A} = 1 - \frac{T_R}{T_A} \end{aligned}$$

$$\frac{-Q_R}{Q_A} = \frac{T_R}{T_A}$$

$$\frac{Q_A}{T_A} = \frac{-Q_R}{T_R}$$

and

$$\begin{array}{ll} \frac{Q_A}{T_A} + \frac{Q'_R}{T_R} < 0 & \frac{Q_A}{T_A} + \frac{Q_R}{T_R} = 0 \\ \sum \frac{Q}{T} < 0 & \sum \frac{Q}{T} = 0 \end{array}$$

But for either cycle

$$\sum \Delta s = 0 = \sum \frac{Q}{T} + \sum \Delta s_{\text{from irreversibilities}}$$

Hence, for the irreversible cycle

$$\Delta s_{\text{from irreversibilities}} > 0 \quad (5-10b)$$

The conclusion is, as before, that the change in entropy for an irreversible process is always greater than  $\sum Q/T$ , while the change of entropy from irreversibilities is always greater than zero, that is, positive in sense

**5-11. The Isolated System.** As the next step in this investigation a cycle and a part of the surroundings affected by the cycle will be defined as an *isolated system*. An *isolated system*, as the name implies, does not have transfers of energy or mass across the boundary. Consider two isolated systems, one system consists of an irreversible cycle with a heat reservoir and a sink, while the other system contains a reversible cycle, heat reservoir, and sink. Suppose these cycles are operated, energy in the form of heat<sup>1</sup> will be converted into available energy and for each system

*Isolated System of Irreversible Cycle  
and Heat Reservoirs*

*Isolated System of Reversible Cycle  
and Heat Reservoirs*

By the same reasoning as in Art 5-10,

$$\sum \left[ \frac{Q}{T} \right]_{\text{cycle}} < 0 \quad (\text{a negative quantity}) \quad \sum \left[ \frac{Q}{T} \right]_{\text{cycle}} = 0$$

But  $Q/T$  at reservoir is (by convention) of opposite sign to that of the cycle, therefore,

$$\sum \left[ \frac{Q}{T} \right]_{\text{reservoirs}} > 0 \quad \sum \left[ \frac{Q}{T} \right]_{\text{reservoirs}} = 0$$

And for one complete operation of the cycle

$$\begin{array}{ll} \sum_{\text{system}} \Delta s = \sum_{\text{reservoirs}} \frac{Q_{\text{rev}}}{T} + \sum_{\text{cycle}} \Delta s & \sum_{\text{system}} \Delta s = \sum_{\text{reservoirs}} \frac{Q_{\text{rev}}}{T} + \sum_{\text{cycle}} \Delta s \\ = (> 0) + 0 & = 0 + 0 \end{array}$$

<sup>1</sup> Technically, this transfer of energy is not heat because it occurs within the system. However, each isolated system can be considered to be made up of two individual systems, and therefore the word heat can be retained, although somewhat illogically.

Therefore,

$$\left. \begin{array}{l} \Sigma \Delta S > 0 \\ \Sigma \Delta E = 0 \end{array} \right\} \begin{array}{l} \text{irreversible} \\ \text{isolated system} \end{array} \qquad \left. \begin{array}{l} \Sigma \Delta S = 0 \\ \Sigma \Delta E = 0 \end{array} \right\} \begin{array}{l} \text{reversible} \\ \text{isolated system} \end{array}$$

Suppose that these cycles are reversed, the available energy stored in the system from the previous forward operations being used to drive the cycles as heat pumps. For the reversible cycle the supply of available energy is sufficient to restore the original condition of the heat reservoir. Nothing has been lost. For the irreversible cycle the supply of available energy is not sufficient to restore the original condition of the heat reservoir. Something has been lost—available energy.

In Example 7, the isolated system contains a work reservoir and water. The net result of the process is a decrease in available energy of the work reservoir and a much smaller increase in available energy of the water.

*Whenever a loss of available energy occurs in an isolated system, it will be found that the entropy and therefore the unavailable energy have increased.* It will be demonstrated in Examples 8 and 9 that the decrease in available energy equals

$$\begin{array}{l} \text{Decrease in available energy of} \\ \text{an isolated system} \end{array} = -T_0 \Sigma \Delta S \quad (5-11)$$

**Example 8.** A pound of ice at 32 F is placed in 5 lb<sub>m</sub> water at a temperature of 80 F. Calculate the change of entropy for this process of an isolated system and the loss of available energy if 32 F is the temperature of the atmosphere.

**Solution.** From Table III (Appendix) the heat of fusion of ice is 144 Btu lb<sub>m</sub><sup>-1</sup> while the specific heat of water is closely 1.0 Btu lb<sub>m</sub><sup>-1</sup> F<sup>-1</sup>.

The equilibrium temperature can be computed for this process at constant enthalpy

$$\begin{aligned} (m\Delta h)_{\text{ice}} + (m\Delta h)_{\text{water}} &= 0 \\ [144 + (t - 32)]1.0 + (t - 80)(1.0)(5) &= 0 \\ -288 + 6t &= 0 \\ t &= 48 \text{ F} \end{aligned}$$

Although, because of the temperature difference, the process is internally irreversible, each constituent, by itself, can be considered to be reversibly heated or cooled. Even if they were not so considered, the initial and end states are known for each constituent, and any path could be selected to find the change in entropy

$$\begin{aligned} \Delta S_{\text{ice}} &= \Delta S_{\text{melting ice at}} + \Delta S_{\text{heating melted ice}} \\ &\qquad \qquad \qquad \text{constant temperature} \qquad \qquad \text{from 32 to 48 F} \\ &= \frac{144}{32 + 460} + c_p \ln \frac{460 + 48}{460 + 32} \\ &= 0.292 + 0.032 \\ &= +0.324 \end{aligned}$$

$$\begin{aligned}
 \Delta S_{\text{water}} &= \Delta S_{\text{cooling from 80 to 48 F}} \\
 &= 5c_p \ln \frac{518}{540} \\
 &= -0.3055 \\
 \Sigma \Delta S_{\text{system}} &= \Delta S_{\text{ice}} + \Delta S_{\text{water}} \\
 &= +0.0185 \text{ Btu/R} \quad \text{Ans.}
 \end{aligned}$$

By Eq (5-11),

$$\begin{aligned}
 \text{Loss of available energy} &= -T_0 \Sigma (\Delta S) \\
 &= -492(0.0185) \\
 &= -9.1 \text{ Btu} \quad \text{Ans}
 \end{aligned}$$

The validity of this answer can be checked by computing the change in available energy for each component of the isolated system just as if the process were reversible. The 5 lb<sub>m</sub> of hot water at 80 F were cooled to 48 F, and therefore heat could have been transferred to a reversible cycle and work could have been obtained of amount equal to the availability of the heat. For this hypothetical process, by Eq (5-9),

$$\begin{aligned}
 Q_{\text{rev}}|_{p-c} = \text{decrease in available energy} &= m \left( \int_{508 \text{ R}}^{540 \text{ R}} c_p dT - T_0 \Delta s \right)_{80 \text{ F}}^{48 \text{ F}} \\
 &= 5 \int_{540 \text{ R}}^{508 \text{ R}} c_p dT - 5T_0 \ln \frac{518}{540} \quad (a) \\
 &= -160 + 150.6 = -9.4 \text{ Btu}
 \end{aligned}$$

The decrease in available energy will have the same value whether or not the process is reversible, but only for the reversible case is the potentiality of producing work preserved.

The ice is melted without increase in available energy because the temperature remains constant. The water is then raised in temperature from 32 to 48 F. The minimum availability of the heat that must be added (hypothetically) to the water is

$$\begin{aligned}
 Q_{\text{rev}}|_{p-c} = \text{increase in available energy} &= \left( \int_{492 \text{ R}}^{508 \text{ R}} c_p dT - T_0 \Delta s \right)_{32 \text{ F}}^{48 \text{ F}} \\
 &= \int_{492 \text{ R}}^{508 \text{ R}} c_p dT - T_0 \ln \frac{518}{492} \quad (b) \\
 &= 16 - 15.7 = 0.3 \text{ Btu}
 \end{aligned}$$

The net change in available energy of the isolated system is

$$\Sigma Q = -9.4 + 0.3 = -9.1 \text{ Btu} \quad \text{Ans}$$

Then, +9.1 Btu of work could have been done by the system and a reversible cycle during the change of state experienced by the system if the process had been reversible. Since the system was isolated, neither work nor heat transfers occurred, and available energy of amount 9.1 Btu was degenerated into unavailable energy.

For an isolated system, the sum of the available and unavailable energies is constant. Then, the net decrease in available energy is equal (but of opposite sign) to the net increase in unavailable energy.

$$\text{Increase in unavailable energy} = +9.1 \text{ Btu}$$

Note that Eqs (a) and (b) can be added together

$$\text{Change in available energy} = -144 - T_0 \ln \frac{40}{10} - 5T_0 \ln \frac{40}{20}$$

and this is recognized to be

$$\begin{aligned} \text{Decrease in available energy} &= -(T_0 \Delta S_{\text{ice}} + T_0 \Delta S_{\text{melted ice}} + T_0 \Delta S_{\text{hot water}}) \\ &= -T_0 \Sigma \Delta S \end{aligned}$$

**Example 9:** For the data of Example 7, show that the increase in unavailable energy for the isolated system is equal to  $T_0 \Sigma \Delta S$

**Solution.** Here the isolated system consists of a work reservoir and water. The decrease in available energy of the reservoir is

$$\text{Decrease in available energy (work reservoir)} = -|W|$$

The increase in available energy of the water because of the rise in temperature is

$$\text{Increase in available energy} = mc_p \Delta T' - T_0 \Delta S \quad (5-8e)$$

Hence, the net change in available energy is

$$\text{Decrease in available energy} = -|W| + mc_p \Delta T' - T_0 \Delta S \quad (c)$$

But the heating effect  $mc_p \Delta T'$  was secured entirely by dissipating the work in friction and turbulence

$$|W| = mc_p \Delta T' \quad (d)$$

When Eq (d) is substituted in Eq (c),

$$\text{Decrease in available energy} = -T_0 \Delta S$$

Therefore,

$$\begin{aligned} \text{Increase in unavailable energy} &= +T_0 \Delta S \\ \Sigma \text{ energy for isolated system} &= 0 \end{aligned}$$

**5-12. The Isolated System (Continued).** Examples 8 and 9 can be summarized by the statement

$$dS]_E \geq 0 \quad \text{for the isolated system} \quad (5-12)$$

and, also,

$$T_0 dS]_E \geq 0 \quad \text{for the isolated system} \quad (5-13)$$

It should be noted that an irreversible process can have a net decrease in entropy if heat is taken away during the irreversible change. But, if the process is isolated, it will always be found that a greater compensating increase in entropy is experienced by the other material taking part in the irreversible change. Clausius recognized this universal loss of available energy in his statement, "*The entropy of the world increases towards a maximum*"

Equation (5-12) was deduced as a consequence of the concept of reversibility. It can now be used to identify an irreversible process

**A process is irreversible if the entropy of the isolated system increases during the process.**

Moreover, a reversible process consists of a continuous series of equilibrium states, and for the reversible process of an isolated system  $dS = 0$ . An irreversible process, on the other hand, is marked by nonequilibrium states, hence, the equilibrium of the state can be judged by Eq (5-12). All irreversible processes have a tendency for spontaneous change to occur. Whenever such a change occurs, the entropy must increase. Example 8 can be used as an illustration for this meaning of the increase in entropy of an isolated system. Here the initial state of the isolated system consists of ice and warm water. Is this an equilibrium state? Obviously it is not, for change of state will occur spontaneously. During this change the entropy increases. The final equilibrium state, when reached, is marked as a state of maximum entropy for a change at constant energy.

**5-13. The System Equation.** In the absence of potential and kinetic effects the First Law can be written for the closed system as

$$\delta Q - \delta W = du \quad (3-7c)$$

When attention is directed only to properties of the system, it is not essential to recognize either heat or work. Equation (3-7c) can be transferred entirely into a system equation by substituting,

$$\begin{aligned} \delta Q_{\text{rev}} &= Tds \\ \delta W_{\text{rev}} &= pdv \end{aligned}$$

When this is done,

$$Tds - pdv = du \quad (5-14a)$$

Equation (5-14a) is valid for either reversible or irreversible processes because all terms of the equation are properties, not affected by events at the boundary. For this equation, however, it should be remembered that  $Tds$  is not heat, nor is  $pdv$  work. Equation (5-14a) also is valid either for flow or for nonflow processes, because the presence of motion does not change the relationships between properties (Art 2-5). This can be realized by developing Eq (5-14a) from the steady-flow equation:

$$\delta Q - \delta W = de_{\text{flow}} \quad (3-12)$$

and

$$\begin{aligned} \delta Q_{\text{rev}} &= Tds \\ -\delta W_{\text{rev}} &= vdp + d(\text{KE}) + d(\text{PE}) \\ de_{\text{flow}} &= du + d(pv) + d(\text{KE}) + d(\text{PE}) \end{aligned}$$

Substitution gives, as before,

$$Tds - pdv = du \quad (5-14a)$$

while it is also evident that, by adding  $d(pv)$  to both sides of the equation,

$$Tds + vdp = dh \quad (5-14b)$$

These are the same equations as for the nonflow system (with the same restriction that  $Tds$  is not heat, nor is  $pdv$  or  $vdp$  work) Upon reflection it must be concluded that this result should have been expected For example, if a steady-flow process has a constant velocity, there will be no change in kinetic energy and no effect upon the properties of Eqs (5-14). If the velocity is used to do reversible work, there will be no change in Eqs (5-14) If the velocity changes reversibly without transfer of heat or work, the effect on Eqs (5-14) is exactly equivalent to that of work reversibly transferred to the system The properties in Eqs (5-14) cannot differentiate between a reversible change of velocity in a flow process and a reversible compression or expansion in a nonflow process If the velocity changes irreversibly, the properties of Eqs (5-14) are affected in the same manner as if heat were transferred to the system *It can be concluded, therefore, that Eqs (5-14) are valid for all processes, reversible or irreversible, that can be shown on a diagram of properties*

It frequently happens that the path of the process is unknown or indeterminate although the initial and final states can be measured Since entropy cannot be directly measured, Eqs (5-14) can be used to calculate the change in this property along any path connecting the two states Essentially this was done in Examples 7 and 8

Equation (5-14a) is the relationship that exists between certain properties of the fluid in flow or nonflow processes In the simplest case of a one-component system in the absence of kinetic and potential energies, the state is defined by two independent intensive properties Equation (5-14a) shows that two of the three *fundamental thermodynamic coordinates*—entropy, specific volume, and internal energy—will always define the state of a simple system However, it is more convenient to use intensive properties that can be directly measured, such as pressure and temperature The means for doing this will be investigated in later chapters

**5-14. The Irreversible Process<sup>1</sup> and the  $\int Tds$**  For a reversible process of a closed system the  $\int pdv$  is work and the  $\int Tds$  is heat What significance is there

<sup>1</sup> This article, like Art 4-8, is not a prerequisite for future material



to these integrals for an irreversible process? A part of this question has already been answered,<sup>1</sup> for

$$\int p dv = W_{\text{irrev}} + F \quad (4-10)$$

It already has been noted (Example 7) that the system is not always able to distinguish between heat and work, for both forms of energy may produce the same effect. This is not surprising since the distinction between heat and work is entirely arbitrary and depends merely upon definitions. Hence, the  $\int T ds$  is the heating effect caused by transfer of heat and dissipation of available energy

$$\int T ds = Q_{\text{irrev}} + F \quad (5-15)$$

In Art. 5-10 reversible and irreversible adiabatic expansion processes were compared. Figure 5-13 illustrates these processes starting from the same initial state.

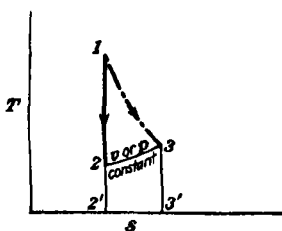


FIG 5-13 Comparison of reversible and irreversible adiabatic expansion processes

The area under the expansion path 1-3 represents the heating effect of the dissipated available energy  $F$ . This area (133'2') measured to some scale equals the amount of available energy so dissipated. As pointed out before,<sup>1</sup> not all this available energy is wasted (lost) because the heating effect increases the availability by changing the path 1-2 to the new path 1-3. The system could now be used as a heat reservoir and cooled from state 3 to state 2, and  $T_2 \Delta s$  would be the net increase in unavailable energy incurred because of the irreversible expansion process.

For the practical case, however, the irreversible process 1-3 is compared<sup>1</sup> with the reversible process 1-2 because it is decidedly inconvenient to use as heat reservoirs the usual commercial systems. Hence, the loss of energy for process 1-3 that was available for path 1-2 is area 233'2'. Note that area 123 represents the increase in available energy of path 1-3 over 1-2. But this is no gain at all because available energy equivalent to area 133'2' was dissipated in the irreversible adiabatic process.

Equation (5-14a) can be derived by substituting Eqs. (4-10) and (5-15) in Eq. (3-7c)

$$\begin{aligned} Q - W &= \Delta u \\ (\int T ds - F) - (\int p dv - F) &= \Delta u \end{aligned}$$

and as before

$$T ds - p dv = du \quad (5-14a)$$

The same result can be obtained for the steady-flow equation by substituting

$$\begin{aligned} -\delta W_{\text{irrev}} &= v dp + d(\text{KE}) + d(\text{PE}) + dF \\ \delta Q_{\text{irrev}} &= T ds - dF \end{aligned}$$

in the First Law equation,

$$\delta Q - \delta W = de_{\text{flow}}$$

to obtain

$$de = T ds - p dv + d(pv) + d(\text{KE}) + d(\text{PE}) \quad (5-16)$$

<sup>1</sup> See Art. 4-8

Each term in this equation can be interpreted as a distinct form of energy

$\int de$	total change of all types of energy
$\int Tds$	change of apparent thermal energy either from irreversibilities or from heat transfers
$-\int pdv$	change of compression energy
$\int d(pv)$	change of flow energy
$\Delta KE$	change in kinetic energy
$\Delta PE$	change in potential energy

Rearranging Eq (5-16),

$$Tds - pdv = de - d(pv) - d(KE) - d(PE)$$

Or, by definition of  $de$ ,

$$de = du + d(pv) + d(KE) + d(PE)$$

and therefore

$$Tds - pdv = du \quad (5-14a)$$

$$Tds + vdp = dh \quad (5-14b)$$

### Problems

1 List to the best of your knowledge all processes or events that the Second Law declares to be impossible

2 Is radiation a violation of the Second Law?

3. If the velocity of a system should increase while the pressure decreased, would this be a violation of the Second Law? Explain How could the problem be stated so that the Second Law would be violated?

4 Can Carnot's main premise be proved true? Could this premise be called the Second Law?

5 Define the terms *heat reservoir* and *heat sink*

6 Prove for definite temperatures of source and sink (a) no engine can be more efficient than a reversible engine, (b) all reversible engines have the same efficiency, (c) efficiency of a reversible engine is independent of the working fluid, (d) a system not receiving work cannot convey heat from a cold to a hot reservoir

7. Twenty Btu of heat are transferred to a reversible engine at a constant temperature of 180 F, and 15 Btu are rejected at a lower but constant temperature. If these are the only heat-transfer processes for the cycle, what is the value of the sink temperature?

8 If 20 Btu of heat are added to a Carnot engine at a temperature of 212 F while 14.6 Btu are rejected at a temperature of 32 F, compute the location of absolute zero

9 A Carnot cycle operates between 300 and 100 F while 100 Btu of heat are supplied. Determine the thermal efficiency, work, heat rejected, and change in entropy for each process

10. A Carnot cycle develops 10 hp while operating between 1000 and 60 F. Determine the thermal efficiency, heat added, and heat rejected

11. For the data of Prob. 9 suppose the engine is reversed and used as a heat pump. Determine the refrigeration ( $Q_A$ )

12. Show that lowering the sink temperature increases the availability of heat. If the sink temperature is lowered below that of the atmosphere (by using a heat pump), can a greater net amount of work be produced?

**13.** A steel rivet at 1800 F and weighing 1 lb<sub>m</sub> is dropped into an insulated bucket containing an equilibrium mixture of 10 lb<sub>m</sub> of water and 5 lb<sub>m</sub> of ice. Determine the final temperature and increase in entropy.

**14.** If in Prob. 13 the steel rivet is the heat reservoir, determine the available and unavailable energy for a sink temperature of 32 F. If the final mixture is considered to be a heat reservoir, determine the available and unavailable energy for a sink temperature of 32 F.

**15.** Explain what is meant by the phrase "reproducible thermal level." Give an example of this.

**16.** Devise an absolute temperature scale that would read 100 degrees at the boiling point of sulphur, and determine the temperatures on this scale for the freezing points of water, tin, and lead.

**17.** A Carnot engine is operated between 1000 and 500 R while a similar engine rejects heat at 1000 R. For equal efficiencies what must be the temperature for heat additions to the second engine?

**18.** In Example 2, an external irreversibility caused a loss in availability. What was gained by the presence of the irreversibility?

**19.** Determine the change in entropy between two states at  $T_1$  and  $T_2$  if both states have the same specific volume and the heat capacity is  $c_v = A + BT + CT^2$ .

**20.** List the uses for the property of entropy.

**21.** A mass of water with constant heat capacity of 1.0 Btu lb<sub>m</sub><sup>-1</sup>R<sup>-1</sup> is warmed from 40 to 180 F. If the corresponding increase in entropy of the water is 2180 ft lb<sub>f</sub> R<sup>-1</sup>, find the mass of fluid involved.

**22.** A gas cycle consists of three reversible processes: *ab* isothermal compression, *bc* constant-pressure expansion, and *ca* reversible adiabatic. Draw this cycle on the *Ts* diagram and indicate areas for (a) heat added, (b) heat rejected, and (c) work done.

**23.** Repeat Prob. 22 for a cycle consisting of the following processes: *ab* isentropic compression, *bc* constant-pressure addition of heat, *cd* constant-volume addition of heat, *de* reversible and adiabatic expansion, *ea* constant-pressure compression.

**24.** For low pressures, the heat capacity of a certain gas is a function only of temperature and is

$$c_p = 0.338 - \frac{0.15(10^3)}{T} + \frac{0.04(10^6)}{T^2}$$

where  $T$  is in degrees Rankine. Compute the change in entropy for a constant-pressure process from 520 to 4000 R.

**25.** Repeat Prob. 22 for a cycle made up of the following processes: *ab* isothermal expansion, *bc* constant-volume addition of heat, *cd* isothermal compression, *da* constant-pressure compression.

**26.** For the data of Probs. 22, 23, and 25 decide whether these are closed or open systems or both.

**27.** Suppose in Prob. 22 that all processes are irreversible but the same series of states is encountered. Do the areas represent heat and work?

**28.** A pound of ice at 32 F is placed in 6 lb<sub>m</sub> of water at 80 F. Calculate the change in entropy for the isolated system and the loss of availability (sink temperature is 32 F).

**29.** A pound of ice at 32 F is placed in 3 lb<sub>m</sub> of water at 70 F. Calculate the change in entropy for the isolated system (sink temperature is 32 F).

**30.** Determine the availability of the heat transferred to the cycle of Example 4 (Assume that the heat is reversibly added to the cycle from two reservoirs, one of finite size and the other of infinite size )

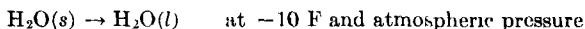
**31** Suppose that in Example 5 combustion of fuel results in a maximum temperature of 3000 R for the gases of combustion. Find the availability for this heat energy and, the maximum possible thermal efficiency of a system receiving heat from this reservoir

**32.** Suppose the cycle of Art. 5-7 is made up of steady-flow processes. Determine the heat and work for each process if kinetic and potential effects are negligible

**33** Water in a constant-pressure container is agitated by a paddle until the temperature rises from 80 to 400 F. Determine (a) the decrease of available energy for the reservoir furnishing the work, (b) the increase in availability of the heat reservoir (the water), (c) the total availability of the water (above 60 F), (d) the loss of availability for the irreversible process of the isolated system

**34.** A stone weighing 50 lb<sub>m</sub> falls from a height of 1,000 ft and strikes an iron plate (100 lb<sub>m</sub>) that has the same temperature as that of the atmosphere (60 F). For the isolated system of stone and plate compute the net loss in available energy. Assume that the heat capacity of stone and plate are equal with value of 0.2 Btu lb<sub>m</sub><sup>-1</sup> R<sup>-1</sup> and that both objects experience the same temperature rise

**35** Water can exist as a supercooled liquid at -10 F. Consider that ice at -10 F spontaneously changes to water at the same temperature while exchanging heat with the environment of -10 F



Prove whether this process is possible, what, however, can readily occur?

### Symbols

$A, B, C$	constants
$c$	heat capacity
$C$	centigrade scale
$e$	energy in general per unit mass
$E$	energy in general
$f$	function
$F$	friction of any kind
$t$	Fahrenheit thermodynamic temperature scale
$K$	Kelvin thermodynamic temperature scale
$KE$	kinetic energy
$l$	distance, length
$m$	mass, also, mass flow rate
$p$	pressure
$PE$	potential energy
$Q$	heat
$R$	electric resistance
$R$	Rankine thermodynamic temperature scale
$S$	entropy
$s$	entropy per unit mass (specific)
$t$	any thermal level, also, thermodynamic temperature
$T$	absolute thermodynamic temperature
$u$	internal energy per unit mass (always in thermal units) (specific)

## Symbols

$v$	specific volume
$W$	work
$a > b$	$a$ greater than $b$
$\ln$	natural logarithm
$\infty$	infinite
$\%$	per cent
$  $	numerical equality
$\approx$	approaches equality

## Greek Letters

$\delta$	(delta)	infinitesimal increment
$\eta$	(eta)	thermal efficiency
$\Delta$	(delta)	difference
$\Sigma$	(sigma)	summation

## Subscripts

$A$	added
$f$	force
irrev	irreversible
$m$	mass
$p$	constant pressure
$R$	rejected
rev	reversible
$v$	constant volume

## Suggested References

- 1 KEENAN, J H "Thermodynamics," John Wiley & Sons, Inc , New York, 1936
- 2 KIEFER, P J , and M C STUART "Thermodynamics," John Wiley & Sons, Inc , New York, 1929

**CLASS ASSIGNMENTS**



## CHAPTER VI

### PROPERTIES OF FLUIDS

The engineer needs complete data on the working fluid that is to be used in a process or cycle. The most usual fluid of all is water, and the properties of water are known to a high degree of precision. For this reason the interrelationships between the properties of water will be studied, although it should be realized that the same types of relationship will be common to all fluids.

**6-1. The  $p$  $v$  $T$  Surface for a Fluid.** The interrelationships between pressure, specific volume, and temperature can be shown on a three-dimensional surface such as that illustrated, in part, by Fig. 6-1. Although this drawing is for water, it can be viewed as a characteristic surface for all fluids (of course, with different numerical values for the coordinates). The coordinates of a point *on* this surface represent the values for pressure, specific volume, and temperature that the fluid must assume if it is to be in a stable equilibrium state. (Conversely, if the properties of the fluid do not dictate a point *on* the surface, the fluid is in a *metastable* state.) There are three regions, labeled *S*, *L*, and *G*, on this model where fluid exists only in a single phase: *solid* (ice), *liquid* (water), and *gas* (steam). In each of these single-phase regions the state of the fluid is defined by any two of the three properties of pressure, specific volume, and temperature, for all of these properties are independent of each other.

Between the single-phase areas are the transitional or two-phase regions where two phases exist in equilibrium: *liquid-vapor*, *solid-vapor*, and *solid-liquid*. The solid-liquid region extends (through *gh*) from *a* to *b*, and the volume at *b* is greater than that at *a*. This is because, when ice melts, the volume decreases. (Most fluids have the opposite characteristic of increasing volume when the solid is liquefied. For these fluids, the solid region will be moved back to *b'*.)

Within the two-phase regions the properties of temperature and pressure are interdependent, for one cannot be changed without changing the other. For this reason the state of the fluid, although defined by two independent properties, cannot be defined by temperature and pressure alone. Specific volume and either temperature or pressure can be used for this purpose.



The specific volume of the two-phase mixture is equal to the sum of the volumes (not specific volumes) of each phase because the *mixture* has unit mass. Hence, if the amount of one phase is increased, the amount of the other phase is correspondingly decreased and the specific volume of the mixture must change because for each phase the specific volumes have different values.

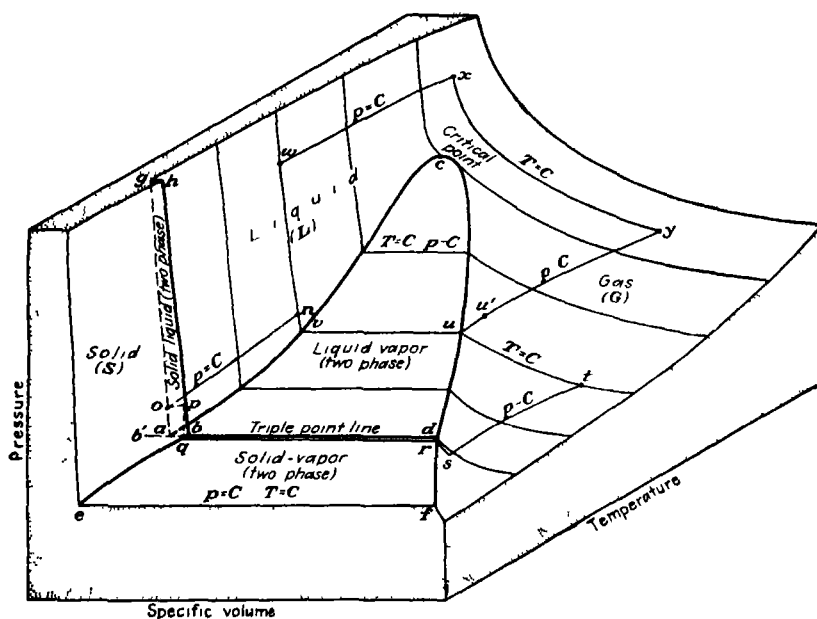


FIG 6-1 The  $p-v-T$  surface for water (not to scale)

Three phases can exist in equilibrium along line  $abd$ , which is the locus of the *triple point*. Here, if the amount of one phase is increased, the amount of the *two* other phases is correspondingly decreased, but the exact amount for each of these two phases is indeterminate. Therefore, the state of a mixture at the triple point cannot be completely defined by the properties of pressure, temperature, and specific volume because an infinite number of mixtures can exist at any point along line  $abd$ . However, inspection of the system equation [Eq (5-14a)] shows that in the absence of potential and kinetic effects the state of the system is determined by the values assumed by two of the three properties of entropy, internal energy, and specific volume.

The liquid from  $u$  to  $v$  is in equilibrium with vapor and is therefore called *saturated liquid*. The locus of single-phase states of saturated

liquid is  $ac$ . Similarly, the locus of single-phase states of *saturated vapor* is  $dc$ . *Saturated vapor* is vapor in equilibrium with saturated liquid. Note that states in the two-phase area,  $acd$ , contain mixtures of saturated vapor and saturated liquid.

A number of processes can be devised to allow a traverse to be made on the surface of Fig 6-1. Consider a liquid at a given pressure and temperature, say point  $n$  in Fig 6-1. When the liquid at state  $n$  is cooled at constant pressure, the volume and temperature decrease while the state shifts toward point  $o$ . Now when the liquid at  $o$  is cooled at constant pressure, ice appears, the volume increases, the temperature remains constant, and the state shifts toward point  $p$  while more and more of the two-phase mixture of liquid and solid turns into ice. The solid at state  $p$  is heated at constant temperature, while pressure is decreased, the volume increases and the state shifts toward  $q$  along the path  $pq$  (lying on the area  $S$ ). The ice at state  $q$  is heated at constant pressure, vapor appears, the volume increases, the temperature remains constant, and the state shifts toward point  $r$  through the two-phase mixture of solid and vapor. At  $r$  the solid has been entirely converted into vapor without the appearance of a liquid phase (sublimation). State  $u$  is attained by traversing the gas region a constant-temperature (expansion) path from  $r$  to  $s$ , a constant-pressure (expansion) path from  $s$  to  $t$ , and a constant-temperature (compression) path from  $t$  to  $u$ . The vapor at state  $u$  is cooled at constant pressure, the temperature remains constant, liquid appears, and the state moves toward  $v$  while the two-phase mixture of liquid and vapor shrinks into liquid. At state  $v$  only liquid is present. The original state  $n$  is restored by isothermal compression of the liquid from  $v$  to  $n$ .

**6-2. The Equilibrium Diagram.** Suppose that all points on Fig 6-1 are projected to the temperature-pressure plane. The resulting plot is called the *equilibrium* or *phase diagram*. It is illustrated by Fig 6-2. All two-phase areas are reduced to lines on a diagram of temperature and pressure because these properties are interdependent during a phase change (phase changes at constant pressure also occur at constant temperature).

Note that the triple point that was a line  $abd$  on Fig 6-1 appears as a point on Fig 6-2. The triple point is often confused with the *ice point*, which is (by definition) the zero of the centigrade scale and  $32^\circ$  on the Fahrenheit scale. At the triple point the pressure of 0.089 psia is exerted entirely by the  $H_2O$ , and therefore the temperature is  $32.018^\circ F$ . The ice point was defined to be  $32^\circ F$  when equilibrium exists between a mixture of ice, water, and air under a total pressure of 14.696 psi. The reason for defining the ice point in this manner was entirely for convenience of test.

Limit  $agh$  slopes to the left for water and to the right for other substances. At extremely high pressures, different phases may be

assumed by the solid Bridgman<sup>1,2</sup> has identified seven different crystalline forms for ice; the regions where they exist are shown in Fig 6-2 Note that the pure substance  $H_2O$  can exist in at least nine different and distinct phases

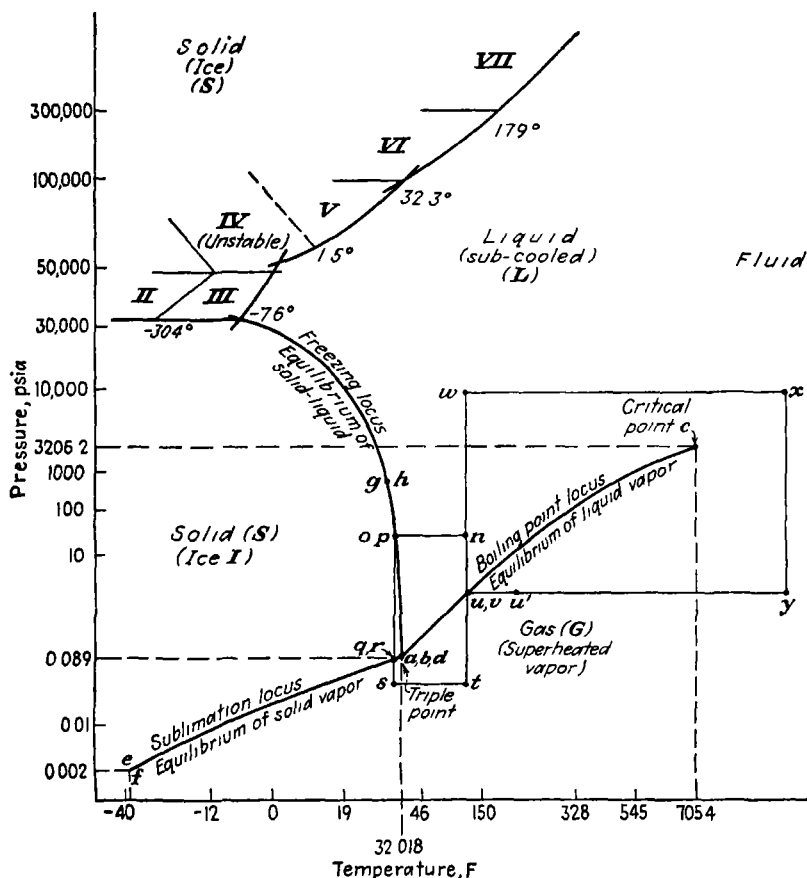


FIG 6-2 Phase diagram for water (not entirely to scale)

Point *c* is called the *critical point* and marks the termination of any distinction between liquid and gaseous phases. If liquid-vapor phases in equilibrium at *w* and confined in a glass cylinder are maintained in equilibrium while the temperature and pressure are raised, the attain-

<sup>1</sup> BRIDGMAN, P. W., High Pressure and Five Kinds of Ice, *J. Franklin Inst.*, **177** (No. 3), 315-332 (1914)

<sup>2</sup> BRIDGMAN, P. W., The Phase Diagram for Water, *J. Chem. Phys.*, **5**, 964-966 (Dec 1937)

ment of state  $c$  will be marked by the disappearance of the meniscus that identified the presence of two phases. In the vicinity of state  $c$ , the properties of the liquid phase and the vapor phase approach each other in similarity, for example, the specific volumes of liquid and gas approach the same value. At state  $c$  all properties of both phases become identical. Note that a single phase of a fluid when confined in a glass container could not be visually recognized to be either a solid, liquid, or gas (unless a change in color occurs with change of phase).

The  $Tp$  diagram shows that the liquid and the gas phases cannot be separately identified when the temperature and pressure are above the critical values. In this region, these two phases merge into one phase without forming a two-phase mixture, and the general name *fluid* is more appropriate than the phase names *liquid* and *gas*.

It is interesting to traverse the fluid region with the glass cylinder and piston. Consider two phases in equilibrium at state  $uv$ . If the pressure is raised while temperature is held constant, the vapor phase disappears as evidenced by disappearance of the liquid meniscus, and the compressed liquid will pass to state  $w$ . Now, if the temperature is raised while pressure is held constant, the state  $x$  can be attained without the appearance of a phase change. Similarly, the state can be changed from  $x$  to  $y$  and  $y$  to  $u'$  without the appearance of two phases. But with the attainment of  $u$ , a liquid phase definitely appears from what was presumably all liquid. Hence, somewhere along the path  $uvwxu'$  the liquid phase must have changed into the gas phase. Since the change occurred without evidence of two phases being present, the exact point cannot be stated where the describing names of gas and liquid became applicable.

The path  $nopqrstn$  followed on Fig. 6-1 is reproduced on Fig. 6-2.

**6-3. Definitions.** At the risk of some duplication a number of new conditions will be defined here.

Limit  $ef$ ,  $abd$ ,  $c$  of Fig. 6-2 is the *vapor pressure curve*.

Liquid in equilibrium with vapor is *saturated liquid*.

Vapor in equilibrium with liquid is *saturated vapor*.

Liquid at a lower temperature than the saturated liquid at the same pressure is called *subcooled liquid* (state  $n$ ).

Vapor at a higher temperature than the saturated vapor at the same pressure is called *superheated vapor* or *gas* (states  $s$ ,  $t$ ,  $u'$ , and  $y$ ).

When a phase change occurs from the solid directly to the gas phase, the process is called *sublimation*. The heat required to effect this change (at constant pressure and temperature) is called the *latent heat of sublimation*. Similarly, the heat required for a phase change from solid to liquid at constant pressure and temperature is called the *latent heat of fusion*, while the heat necessary to vaporize liquid into gas at constant pressure and temperature is called the *latent heat of*

vaporization. The term *latent heat* is used because no rise in temperature accompanies the transfer of heat during a phase change

**6-4. Pressure-Specific-volume Diagram.** A diagram of pressure and specific volume (Fig 6-3) can be obtained by projecting all points of Fig 6-1 over to the  $pv$  plane. The regions  $S$ ,  $L$ , and  $G$  correspond

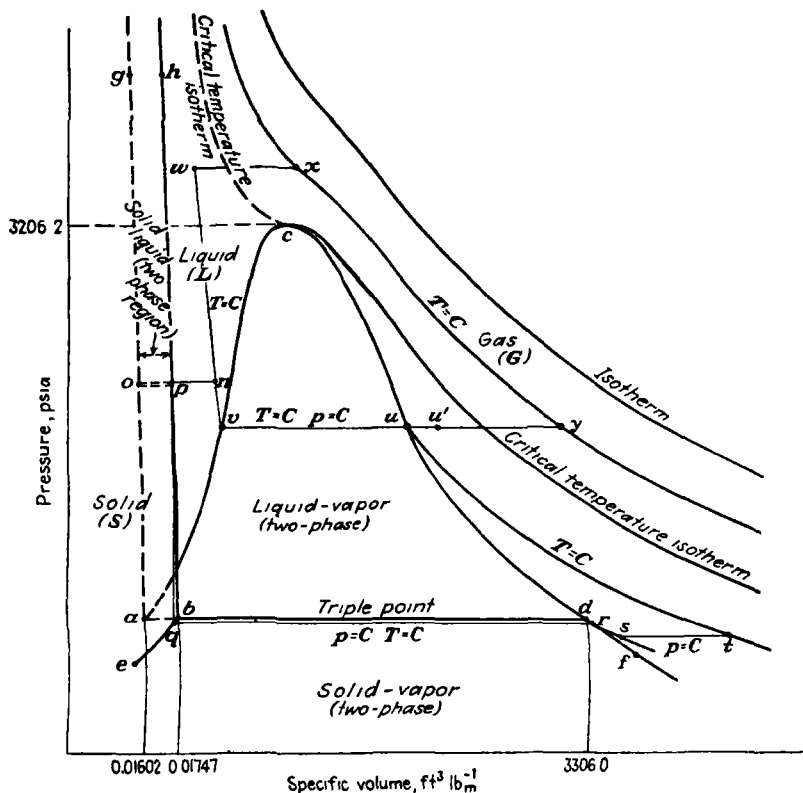


Fig 6-3 Pressure specific-volume diagram for water (not to scale)

to the phases indicated by the same letters in Fig 6-2. Note that the triple point on the pressure-volume diagram is a line while the phase boundaries of Fig 6-2 become *areas*. Since the phase change from solid to liquid is marked by a decrease in volume, the liquid region on a plane diagram lies to some extent under the solid-liquid region ( $abgh$ ).

Figure 6-3 illustrates that, for temperatures above the critical temperature, compression of a gas (without cooling) will not cause the appearance of two phases signifying condensation to the liquid state. Because of this it is often stated that a gas with temperature above the

critical temperature cannot be liquified by compression. It would be better to say that a liquid and a gas cannot be distinguished from each other under these conditions.

The paths *nopqrstuvw* and *uvwxyu'u* are reproduced on this diagram to facilitate study.

**6-5. The Two-phase Mixture.** The relative amounts of each phase that are present in a two-phase mixture depend on the *quality* of the mixture. The *quality* of a two-phase mixture is equal to the ratio of the mass of vapor to the total mass of mixture. Although defined as a ratio, it is frequently used as a percentage. Saturated liquid is zero quality or 0 per cent moisture. Saturated vapor is 100 per cent vapor and 0 per cent moisture. A quality of 0.60 signifies that the mixture consists of 60 per cent vapor and 40 per cent liquid. The letter *x* will be used to designate the quality.

$$x = \frac{\text{mass of vapor}}{\text{mass of mixture}}$$

Since the pound mass will be the usual unit,

$$1 \text{ lb}_m \text{ mixture of } x \text{ quality} = x \text{ lb}_m \text{ vapor} + (1 - x) \text{ lb}_m \text{ liquid} \quad (a)$$

The *specific* values (that is, values for 1 lb<sub>m</sub>) for the extensive properties of volume, enthalpy, entropy, and others can be determined by Eq. (a) for the mixture. (The state of saturated liquid is denoted by the subscript *f* and that for the saturated vapor by the subscript *g*.)

$$\left. \begin{aligned} v_{\text{at quality } x} &= v_x = xv_g + (1 - x)v_f \\ h_x &= xh_g + (1 - x)h_f \\ s_x &= xs_g + (1 - x)s_f \end{aligned} \right\} \quad (b)$$

The change in these properties during the phase change is shown by the subscript *fg* or

$$\left. \begin{aligned} h_g - h_f &= h_{fg} \\ v_g - v_f &= v_{fg} \\ s_g - s_f &= s_{fg} \end{aligned} \right\} \quad (c)$$

Equations (b) [by the use of Eq. (c)] can be converted to

$$\left. \begin{aligned} v_x &= v_f + xv_{fg} \\ h_x &= h_f + xh_{fg} \\ s_x &= s_f + xs_{fg} \end{aligned} \right\} \quad (6-1)$$

It should be understood that values for the saturated properties are selected for the conditions of pressure and temperature present for the two-phase state.

**6-6. Tables of Properties.** Complete data are not available for most fluids used in engineering. The properties of a few of the more common fluids have been the object of experiment for many years, and the properties of water have been evaluated to a high degree of accuracy. The data for water are compiled in volumes called the *Steam Tables*, an example of which is "Thermodynamic Properties of Steam"<sup>1</sup> by Keenan and Keyes. This particular volume is used so extensively in engineering that a résumé of the contents will be made in the following section.<sup>2</sup>

In Table 1 the data are arranged with temperature as the independent variable. Values are given from 32 F to the critical point of 705.4 F. In Table 2 pressure is used as the independent variable with values ranging from 0.25 in. Hg to the critical point of 3206.2 psi. These tables locate the vapor-pressure curve *adc* in Fig. 6-2.

Table 1. Saturation Temperatures

Temp Fahr t	Abs Pressure		Specific Volume			Enthalpy			Entropy			Temp Fahr t
	Lb		Sat			Sat			Sat			
	Sq	In	Liquid	Evap	Vapor	Liquid	Evap	Vapor	Liquid	Evap	Vapor	
	p	p	$v_f$	$v_{fg}$	$v_g$	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_{fg}$	$s_g$	
32°	0.08854	0.1803	0.01602	3306	3306	0.00	1075.8	1075.8	0.0000	2.1877	2.1877	32°
35	0.09995	0.2035	0.01602	2947	2947	3.02	1074.1	1077.1	0.0061	2.1709	2.1770	35
60	0.2563	0.5218	0.01604	1206.6	1206.7	28.06	1059.9	1098.0	0.0555	2.0393	2.0948	60
80	0.5069	1.0321	0.01608	633.1	633.1	48.02	1048.6	1096.6	0.0932	1.9428	2.0360	80
100	0.9492	1.9325	0.01613	350.3	350.4	67.97	1037.2	1105.2	0.1295	1.8531	1.9826	100
705.4	3206.2		0.0503	0	0.0503	902.7	0	902.7	1.0580	0	1.0580	705.4

Abstracted from "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc., New York, 1936, by permission.

Table 2. Saturation Pressures

Saturated Properties of Water															Abs		
Press		Specific Volume				Enthalpy				Entropy				Internal Energy			Press
Lb	Temp	Sat		Sat	Sat	Sat	Sat	Sat	Sat	Sat	Sat	Sat	Sat	Sat	Sat	Lb.	
Sq	In	Fahr	Liquid	Evap	Vapor	Liquid	Evap	Vapor	Liquid	Evap	Vapor	Liquid	Evap	Vapor	Sq	In	
p	t	$T_f$	$v_f$	$v_{fg}$	$v_g$	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_{fg}$	$s_g$	$u_f$	$u_{fg}$	$u_g$	p		
3.0	141	48	0	0.01630	118.71	109.37	1013.2	1122.6	0.2008	1.6855	1.8863	109.36	947.3	1056.7	3.0		
15	213	03	0	0.01672	26.29	181.11	969.7	1150.8	0.3135	1.4415	1.7540	181.06	896.7	1077.8	15		
50	281	01	0	0.01727	8.515	250.09	924.0	1174.1	0.4110	1.2474	1.6585	249.93	845.4	1095.3	50		
100	327	81	0	0.01774	4.432	298.40	888.8	1187.2	0.4740	1.1286	1.6028	298.08	807.1	1105.2	100		
144	355	21	0	0.01805	3.134	327.13	866.3	1193.4	0.5097	1.0631	1.5728	326.65	783.3	1109.9	144		
180	358	42	0	0.01809	3.015	330.51	863.6	1194.1	0.5138	1.0556	1.5694	330.01	780.5	1110.5	180		
1,000	544	61	0	0.0216	0.4240	0.4456	542.4	849.4	1.191	8.0	7.430	0.6467	1.3897	538.4	1109.4	1,000	
3,206.2	705	40	0	0.0503	0	0.0503	902.7	0	902.7	1.0	580.0	0	1.0580	872.9	872.9	3,206.2	

Abstracted from "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc., New York, 1936, by permission.

The datum for enthalpy and entropy arbitrarily is designated to be the state of saturated liquid at 32 F.

**Example 1:** What is the internal energy of 1 lb<sub>m</sub> of saturated water at 32 F?

<sup>1</sup> John Wiley & Sons, Inc., New York, 1936.

<sup>2</sup> Other tables are available for the properties of engineering fluids. See references at the end of this chapter.

**Solution:** Steam Table 1 does not list values of internal energy. However, internal energy can always be computed from the defining equation for enthalpy

$$h = u + \frac{pv}{J} \quad (2-6b)$$

From Steam Table 1

$$\begin{aligned} h_f &= 0.00 \\ p &= 0.08854 \text{ psi} \\ v_f &= 0.01602 \text{ ft}^3 \\ u &= h - \frac{pv}{J} \\ &= 0.00 - \frac{0.08854(144)(0.01602)}{778.16} \\ &= -0.0002625 \text{ Btu/lb}_m \end{aligned}$$

The minus sign is a consequence of the arbitrary datum assigned to enthalpy

**Example 2.** Calculate the entropy change during vaporization from the saturated-liquid state at 35 F to the saturated-vapor state and compare with the table value

**Solution:** From Steam Table 1, at 35 F,

$$h_{fg} = 1074.1 \text{ Btu/lb}_m$$

The defining equation for entropy is

$$\Delta s = \int \frac{dQ}{T} \Big|_{\text{rev}}$$

Since this is a constant-temperature and also a constant-pressure change,

$$\Delta s = \left[ \frac{Q}{T} \right]_{\text{rev}} = \frac{h_{fg}}{T} = \frac{1074.1}{35 + 459.6} = 2.1709 \text{ Btu/lb}_m \text{ R} \quad \text{Ans}$$

Or the same equation can be derived from the system equation

$$Tds + vdp = dh \quad (5-14b)$$

and for this constant-pressure change

$$dp = 0$$

Hence,

$$ds = \frac{dh}{T}$$

Since the temperature is constant,

$$\Delta s = \frac{h_{fg}}{T}$$

**Example 3.** What are the specific volume and specific enthalpy of a two-phase mixture of 35 per cent quality if the pressure is 3 psi?

**Solution.** From Steam Table 2, for  $p = 3$  psi,

$$\begin{aligned} v_f &= 0.01630 \text{ ft}^3/\text{lb}_m \\ v_g &= 118.71 \text{ ft}^3/\text{lb}_m \\ h_f &= 109.37 \text{ Btu/lb}_m \\ h_{fg} &= 1013.2 \text{ Btu/lb}_m \end{aligned}$$



By Eq (6-1),

$$\begin{aligned}
 v_x &= v_f + x v_{fg} \\
 &= 0.01630 + x(118.71 - 0.01630) \\
 &\approx 0.35(118.71) \\
 v_x &= 41.5 \text{ ft}^3/\text{lb}_m \quad \text{Ans} \\
 h_x &= h_f + x h_{fg} \\
 h_x &= 109.37 + 0.35(1013.2) \\
 h_x &= 463.4 \text{ Btu/lb}_m \quad \text{Ans}
 \end{aligned}$$

In Steam Table 3 the two independent properties of pressure and temperature are used to define the state of a single-phase system of gas. Steam Table 3 presents values from 1 psia and 120 F to 5500 psia and 1600 F. This range covers in part region *G* of Figs 6-1, 6-2, and 6-3.

**Table 3. Superheated Vapor**

Abs. Press. Lb /Sq. In. (Sat. Temp.)	Sat. Liquid	Sat Vapor	Temperature—Degrees Fahrenheit						
			260°	300°	360°	400°	460°	500°	
<b>14.696</b> (212.00)	<b>v</b> 0.02	26.80	28.85	30.53	33.03	34.68	37.14	38.78	
	<b>h</b> 180.1	1150.4	1173.8	1192.8	1221.1	1239.9	1268.2	1287.1	
	<b>s</b> 0.3120	1.7566	1.7902	1.8160	1.8518	1.8743	1.9060	1.9261	
 <b>138</b> (351.91)	 <b>v</b> 0.018	3.264			3.309	3.521	3.821	4.013	
	<b>h</b> 323.6	1192.7			1197.8	1221.4	1254.3	1275.4	
	<b>s</b> 0.5054	1.5763			1.5825	1.6106	1.6476	1.6700	
 <b>140</b> (353.02)	 <b>v</b> 0.018	3.220			3.258	3.468	3.764	3.954	
	<b>h</b> 324.8	1193.0			1197.3	1221.1	1254.1	1275.2	
	<b>s</b> 0.5069	1.5751			1.5804	1.6087	1.6458	1.6683	
 <b>144</b> (355.21)	 <b>v</b> 0.018	3.134			3.160	3.366	3.655	3.840	
	<b>h</b> 327.1	1193.4			1196.5	1220.4	1253.6	1274.8	
	<b>s</b> 0.5097	1.5728			1.5765	1.6050	1.6423	1.6649	
 <b>150</b> (358.42)	 <b>v</b> 0.018	3.015			3.023	3.223	3.502	3.681	
	<b>h</b> 330.5	1194.1			1195.1	1219.4	1252.9	1274.1	
	<b>s</b> 0.5138	1.5694			1.5706	1.5995	1.6372	1.6599	
 <b>1000</b> (544.61)	 <b>v</b> 0.0216	0.4456							
	<b>h</b> 542.4	1191.8							
	<b>s</b> 0.7430	1.3897							

Abstracted from "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc., New York, 1936, by permission.

**Example 4:** How much heat must be transferred to raise the temperature of steam from the saturation temperature to 500 F if the pressure is constant at 144 psia?

**Solution:** For a constant-pressure (and reversible) process the heat added equals the change in enthalpy

$$Q_{\text{rev}}|_{p=\text{C}} = h_2 - h_1 \quad (4-4)$$

From Steam Table 3,

$$\begin{array}{lll} 144 \text{ psia} & 355.21 \text{ F} & h_g = 1193.4 \text{ Btu/lb}_m \\ 144 \text{ psia} & 500 \text{ F} & h = 1274.8 \text{ Btu/lb}_m \\ & Q_{\text{rev}} = \Delta h & \\ & = 81.4 \text{ Btu/lb}_m & \text{Ans} \end{array}$$

**Example 5:** Assume that the heat transferred in Example 4 was a measured quantity and the entropy change for the process is to be calculated

**Solution:** The average heat capacity can be calculated

$$\begin{aligned} Q_{\text{rev}}|_{p-c} &= c_p \Delta t = 81.4 \text{ Btu/lb}_m & (\text{Example 4}) \\ c_p &= \frac{Q_{\text{rev}}}{\Delta t} = \frac{81.4}{144.8} \\ c_p &= 0.562 \text{ Btu/lb}_m \text{ F} \end{aligned}$$

The change in entropy can be calculated from

$$\begin{aligned} \Delta s &= c_p \ln \frac{T_2}{T_1} & (5-4) \\ &= 0.562 \ln \frac{959.6}{814.8} \\ &= 0.0921 \text{ Btu/lb}_m \text{ F} \end{aligned}$$

The entropy at the initial state is (Steam Table 3)

$$s_1 = 1.5728$$

and

$$\begin{aligned} s_2 &= s_1 + \Delta s \\ s_2 &= 1.6649 \text{ Btu/lb}_m \text{ F} & \text{Ans} \end{aligned}$$

The value listed in Steam Table 3 at 144 psia is

$$s_2 = 1.6649 \quad \text{Ans}$$

The answer checks the table, although it should be realized that this method is an approximation

**Example 6:** How much heat must be transferred to 1 lb<sub>m</sub> of steam in a constant-volume container to raise the pressure from 144 psia to 150 psia? The initial temperature is 360 F

**Solution:** From Steam Table 3 for the initial conditions

$$\begin{aligned} p_1 &= 144 \text{ psia} \\ t_1 &= 360 \text{ F} \\ v_1 &= 3.160 \text{ ft}^3/\text{lb}_m \\ h_1 &= 1196.5 \text{ Btu/lb}_m \end{aligned}$$

The heat added at constant volume is equal to the change in internal energy [Art 4-7 and Eq (4-7)] Since this property is not listed in Steam Table 3, it must be computed in the manner illustrated in Example 1

$$\begin{aligned} u_1 &= h_1 - \frac{p_1 v_1}{J} \\ &= 1196.5 - \frac{144(144)3.160}{778.16} \\ &= 1112.2 \text{ Btu/lb}_m \end{aligned}$$

The volume and pressure at the end of the process are known, hence, interpolation can be made in Steam Table 3 between temperatures of 380 and 390 F at a pressure of 150 psia to find

$$h_2 = 1211.4 \text{ Btu/lb}_m$$

Solving for internal energy gives

$$\begin{aligned} u_2 &= 1211.4 - \frac{150(144)3.160}{778.16} \\ &= 1123.6 \text{ Btu/lb}_m \end{aligned}$$

and

$$\begin{aligned} Q_{\text{rev}}]_{v-c} &= u_2 - u_1 = 1123.6 - 1112.2 \\ &= 11.4 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

The data in Steam Table 4 for the single-phase state of compressed liquid are tabulated for the independent properties of pressure and temperature. Difference values are given for each property from the saturation state to the state in question.

Table 4 Compressed Liquid  
Temperature—Degrees Fahrenheit

		32°		100°	200°	300°
		p	0 08854	0 9492	11 526	67 013
Saturated		$v_f$	0 016022	0 016132	0 016634	0 017449
Liquid		$h_f$	0	67 97	167 99	269 59
		$s_f$	0	0 12948	0 29382	0 43694
Abs Press. Lb /Sq. In (Sat. Temp )						
200 (381 79)	( $v - v_f$ )	$10^6$	-1 1	-1 1	-1 1	-1 1
	( $h - h_f$ )		+0 61	+0 54	+0 41	+0 23
	( $s - s_f$ )	$10^3$	+0 03	-0 05	-0 21	-0 21
400 (444 59)	( $v - v_f$ )	$10^6$	-2 3	-2 1	-2 2	-2 8
	( $h - h_f$ )		+1 21	+1 09	+0 88	+0 61
	( $s - s_f$ )	$10^3$	+0 04	-0 16	-0 47	-0 56
600 (486 21)	( $v - v_f$ )	$10^6$	-3 5	-3 2	-3 4	-4 3
	( $h - h_f$ )		+1 80	+1 67	+1 31	+0 97
	( $s - s_f$ )	$10^3$	+0 07	-0 27	-0 74	-0 94
800 (518 23)	( $v - v_f$ )	$10^6$	-4 6	-4 0	-4 4	-5 6
	( $h - h_f$ )		+2 39	+2 17	+1 78	+1 35
	( $s - s_f$ )	$10^3$	+0 10	-0 40	-0 97	-1 27
1000 (544 61)	( $v - v_f$ )	$10^6$	-5 7	-5 1	-5 4	-6 9
	( $h - h_f$ )		+2 99	+2 70	+2 21	+1 75
	( $s - s_f$ )	$10^3$	+0 15	-0 53	-1 20	-1 64

Abstracted from "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc., New York, 1936, by permission.

**Example 7:** Water is isentropically compressed in a flow process from the saturated state at 100 F to a pressure of 1,000 psia. How much work is required?

How much work is required if the efficiency of the pump is 60 per cent (of the reversible value)?

**Solution:** Steam Table 4 indicates that the entropy at 1,000 psia and 100 F is less than the initial (saturated) value at 100 F. Therefore, during the isentropic compression (Fig. A) the temperature of the water must have increased to some extent. Interpolation can be made at 1,000 psia between 100 and 200 F for the state where the entropy is equal in value to the initial value

$$s_f = 0.12948$$

Although the accuracy of this interpolation is questionable because of the wide difference in temperature, however, interpolation shows

$$s_1 = s_2 = 0.12948 \quad \Delta t = 0.32 \text{ F}$$

And the temperature<sup>1</sup> after compression

is

$$t_2 = 100.32 \text{ F}$$

Hence, the temperature rise is negligibly small, and the temperature after compression can be assumed to be equal to the initial temperature for most problems. In the same manner, the enthalpy corresponding to this temperature and at a pressure of 1,000 psia is found to be

$$\begin{aligned} h_2 &= h_f + \Delta h_{t-c} + \Delta h_{p-c} \\ &= 67.97 + 2.70 + 0.3 \end{aligned}$$

(Here the 0.3 Btu could have been neglected.) The work is

$$\begin{aligned} W_{\text{rev}} &= h_1 - h_2 \\ &= -3.0 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

If the efficiency of the actual pump is 60 per cent, then the work required is

$$\eta_{\text{pump}} = \frac{\text{ideal work}}{\text{actual work}} = \frac{W_{\text{isen}}}{W_{\text{actual}}}$$

or

$$\begin{aligned} W_{\text{actual}} &= \frac{-3.0}{0.60} \\ &= -5.0 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

Hence, for the actual pump the enthalpy of the liquid will be increased because of friction and turbulence. This heating effect will cause a pronounced rise in temperature when compared with the temperature rise of the reversible pump. Interpolating again between 100 F and 200 F at 1,000 psia but noting that the heat capacity is closely  $1 \text{ Btu lb}_m^{-1} \text{ F}^{-1}$  and that  $2 \text{ Btu lb}_m^{-1}$  of energy is dissipated in turbulence will give

<sup>1</sup> Inspection of Fig. 6-4 shows that, for water at 39 F, isentropic compression will result in no rise in temperature

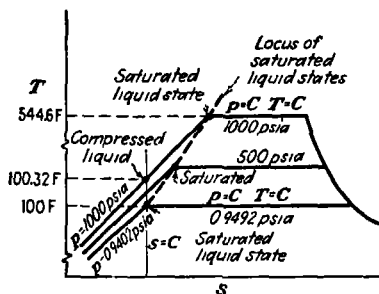


FIG. A Exaggerated  $Ts$  diagram to show compression of saturated water to 1000 psia (subcooled at 1000 psia)



Since the volume does not change greatly,

$$\begin{aligned} W_{\text{rev}} &\approx -v(p_2 - p_1) \\ &\approx -\frac{0.01613(144)(1000 - 0.9)}{778.16} \\ &\approx -2.99 \text{ Btu/lb}_m \quad \text{Ans.} \end{aligned}$$

But this same equation can be obtained by assuming that the work is necessary only to increase the flow energy of the fluid. The small amount of work spent in compressing the liquid was noted in Art. 3-6b

$$\begin{aligned} W_{\text{comp}} &= \int p dv \\ &\approx p_{\text{avg}} \Delta v \\ &\approx \left( \frac{1000.9}{2} \right) (0.000051) \frac{144}{778.16} \\ &\approx 0.0053 \text{ Btu/lb}_m \end{aligned}$$

Hence, the work supplied to the usual liquid pump is used to increase the flow energy of the fluid, and only a negligible portion of the work is used to compress the fluid.

**6-7. The Temperature Entropy Diagram.** A diagram of temperature and entropy when constructed from the Steam Tables would appear similar to Fig. 6-4. The state of the subcooled liquid will apparently be on the saturated-liquid line because of the proximity of constant-pressure lines for the liquid phase in this region. The little effect that compression has on the temperature of the liquid was illustrated in Example 7.

**Example 8.** Water at a temperature of 100.32 F and a pressure of 1,000 psia is to be heated in a steady-flow process to the state of dry saturated steam at the same pressure. How much heat must be transferred?

**Solution:** For the liquid phase, Steam Tables 1 and 2 give only saturated values. However, the enthalpy of subcooled water at the state given in this problem corresponds to that of Example 7. From this example,

$$p_1 = 1,000 \text{ psia} \quad t_1 = 100.32 \text{ F} \quad h_1 = 70.97 \text{ Btu/lb}_m$$

From Steam Table 2,

$$p_2 = 1,000 \text{ psia} \quad t_2 = 544.61 \text{ F} \quad h_2 = 1191.8 \text{ Btu/lb}_m$$

For this steady-flow process Eq. (3-15) shows that

$$Q_{\text{rev}} = h_2 - h_1 = 1120.8 \text{ Btu/lb}_m \quad \text{Ans.}$$

The area representing this quantity of heat is laid out in Fig. B as  $a'abcc'$ .

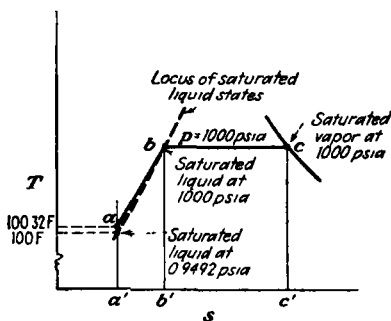


FIG. B Constant pressure heating process (at  $p = 1000 \text{ psia}$ )

**Example 9:** What significance is there to the area under the saturated liquid line on the  $Ts$  diagram (Fig. B, Example 8)?

**Solution:** Since any area on a  $Ts$  diagram represents a reversible transfer of heat, this area represents the heat transferred during a reversible process wherein the pressure increases continuously although all states are saturated states. The First Law can be applied to such a process executed by a closed system

$$Q - W = \Delta u = u_2 - u_1$$

and

$$W_{\text{rev}} = \int p dv$$

Hence,

$$Q_{\text{rev}} = u_2 - u_1 + \int_1^2 p dv$$

Note that  $Q$  is neither  $\Delta u$  nor  $\Delta h$ . This equation can be graphically solved by measuring the  $\int p dv$  on a  $pv$  diagram.

The same answer can be obtained in a slightly different form by proposing that the process be a reversible flow process. For this case the First Law shows

$$Q - W = \Delta h$$

and

$$W_{\text{rev}} = - \int v dp$$

Hence,

$$Q_{\text{rev}} = h_2 - h_1 - \int_1^2 v dp$$

This equation can be evaluated in the same manner as for the closed-system equation [and both equations can be directly obtained from the system equation (5-14)]

**6-8. The Mollier Diagram.** A convenient diagram of properties is the enthalpy-entropy diagram (Fig. 6-5) proposed by and named after *Mollier*. This chart is widely used for industrial problems involving high-pressure steam; hence, the usual version presents only the part of the two-phase region that will normally be of value. Studying Fig. 6-5, note that constant-pressure lines incline upward and to the right and that within the two-phase region they are also lines of constant temperature. From the saturated-vapor line originate curved isothermals that approach a horizontal limit some distance from the saturation line. Lines of constant moisture and lines of constant superheat cross the pressure lines at approximately 90 deg. In the low-pressure region the constant-pressure lines are constructed for units of inches of mercury as well as units of pounds per square inch.

**Example 10:** Steam at a pressure of 144 psia and a temperature of 400 F enters an ideal turbine and leaves at a pressure of 3 psia under conditions of steady

flow How much work is delivered (a) if the process is adiabatic and reversible and entering and leaving kinetic energies are negligible, (b) if the turbine is irreversible and only 70 per cent of the isentropic work is obtained?

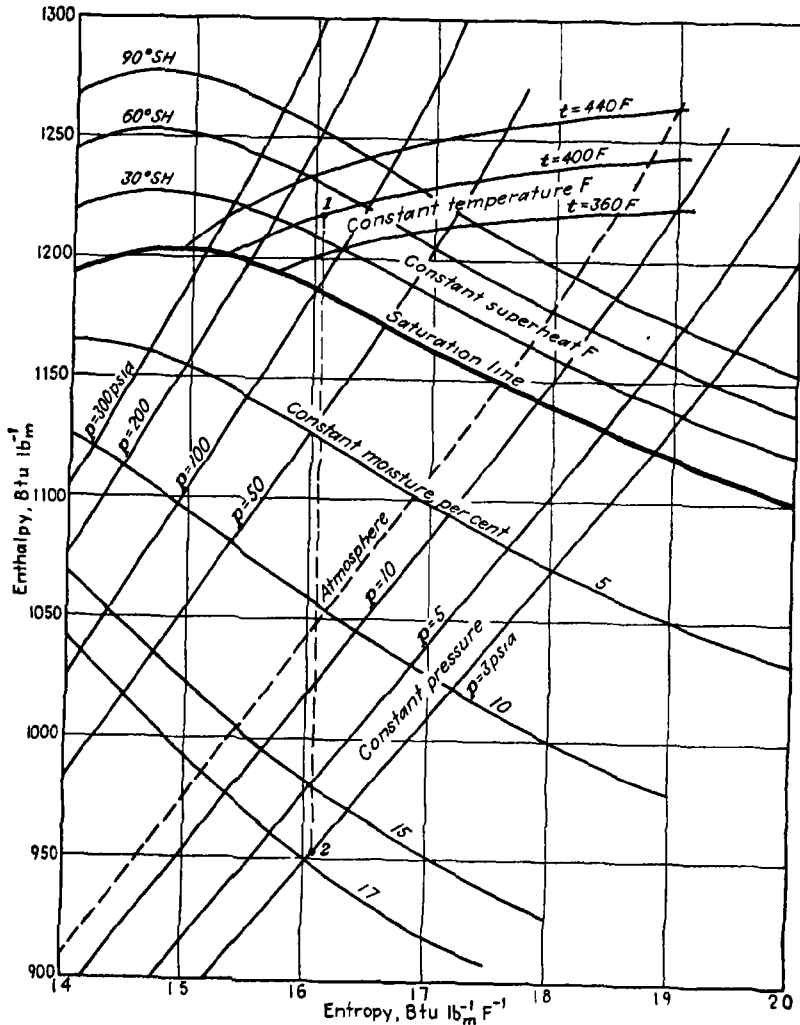


FIG 6-5 Mollier diagram ( $h_s$ ) for steam

**Solution:** a The work done by a steady-flow system under these conditions is (Arts 3-6f and 5-10)

$$W_{rev} = (h_1 - h_2)_{isen}$$



The properties of the steam entering the turbine are obtained from Steam Table 3.

$$\begin{aligned}h_1 &= 1220.4 \text{ Btu/lb}_m \\s_1 &= 1.6050 \text{ Btu/lb}_m \text{ R}\end{aligned}$$

At exit the known properties are

$$\begin{aligned}s_2 &= 1.6050 \text{ Btu/lb}_m \text{ R} \\p_2 &= 3 \text{ psia}\end{aligned}$$

Inspection of Steam Table 2 shows that for this value of entropy the steam must be a two-phase mixture. The quality must be calculated from Eq. (6-1)

$$s_2 = s_f + x s_{fg}$$

(Values of  $s_f$  and  $s_{fg}$  are obtained from Steam Table 2 while  $s_2$  is known)

$$\begin{aligned}1.6050 &= 0.2008 + x(1.6855) \\x &= 0.835\end{aligned}$$

Since the quality is known, the enthalpy can be calculated

$$\begin{aligned}h_2 &= h_f + x h_{fg} \\&= 109.37 + (0.835)(1013.2) \\&= 956.4 \text{ Btu/lb}_m\end{aligned}$$

and the work can be found from the change in enthalpy

$$\begin{aligned}W_{\text{rev}} &= h_1 - h_2 = 1220.4 - 956.4 \\&= 264 \text{ Btu/lb}_m \quad \text{Ans}\end{aligned}$$

This problem is greatly simplified by use of a Mollier diagram. The initial conditions can be located on this chart as shown in Fig. 6-5 for the data of Example 10. From the initial state to the end state is a process at constant entropy, and therefore following a vertical path from point 1 down to the known pressure line enables the enthalpy of state 2 to be directly read from the ordinate without calculation for the quality.

b. The irreversible process will deliver

$$\begin{aligned}W &= 0.70(264) \\&= 184.8 \text{ Btu/lb}_m \quad \text{Ans}\end{aligned}$$

The final state of the steam can also be located on the Mollier diagram since the pressure and enthalpy are known

$$\begin{aligned}h_2' &= h_1 - W \\&= 1220.4 - 184.8 \\&= 1035.6 \text{ Btu/lb}_m\end{aligned}$$

and

$$p = 3 \text{ psia}$$

**6-9. The Throttling Calorimeter.** Although the state of a one-phase system is completely described by measuring the independent properties of temperature and pressure, for a two-phase system temperature and pressure are no longer independent, and some other

property such as enthalpy or internal energy must therefore be measured before the state can be determined. However, measurements of the intensive properties of temperature and pressure are more easily and more precisely made than measurements of extensive properties, hence, it is preferable to devise a means to use these intensive properties as indicators of the state of a two-phase system. In Fig 6-6 are shown the elements of a Mollier diagram, and point *a* represents the state of a two-phase system. The pressure and temperatures of *a* do not determine the state because any other state such as *x* would have the same values for these properties. Now, if the fluid at state *a* passes to state *b* by a process at constant enthalpy, state *b* is defined by pressure and temperature alone because only one phase will be present. If a constant enthalpy process is devised that will enable state *b* to be attained, then state *a* can be found from calculation because the enthalpy at *a* is equal to that of *b* and this property along with the independent property of pressure (or temperature) determines the state of a two-phase system.

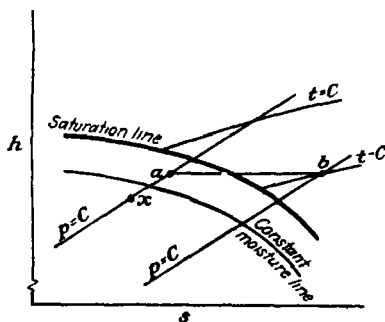


Fig 6-6 Throttling (calorimeter) process on *h-s* diagram

The constant-enthalpy process can be closely approached by use of a *throttling calorimeter* (Fig 6-7). A sampling tube *s* is inserted into a vertical pipe wherein (preferably) the flow is downward<sup>1</sup>. A representative sample of the steam enters the tube and expands through an orifice *o* to the lower pressure existing in the calorimeter (usually atmospheric). The temperature and pressure of the steam in the calorimeter can be measured quite easily.

When the steady-flow equation is applied to the system described by Fig 6-7 for this Joule-Thomson expansion (Art 3-6e),

$$h_a + \frac{V_a^2}{2Jg_c} + Q = h_b + \frac{V_b^2}{2Jg_c} + W$$

In this throttling process *W* is zero and *Q* can approach zero by proper insulation, while the entering and leaving velocities can be equalized by proper selection of pipe sizes; accordingly,

$$h_a = h_b$$

<sup>1</sup> This does not disturb the distribution of particles of water throughout the vapor to as great a degree as other positions of the pipe

Measuring  $t_b$  and  $p_b$  enables  $h_b$  to be determined from Steam Table 3. Since  $h_b = h_a$ , measurement of  $p_a$  or  $t_a$  completes the information necessary to define the state of  $a$  that can now be located on a Mollier diagram or determined by calculation.

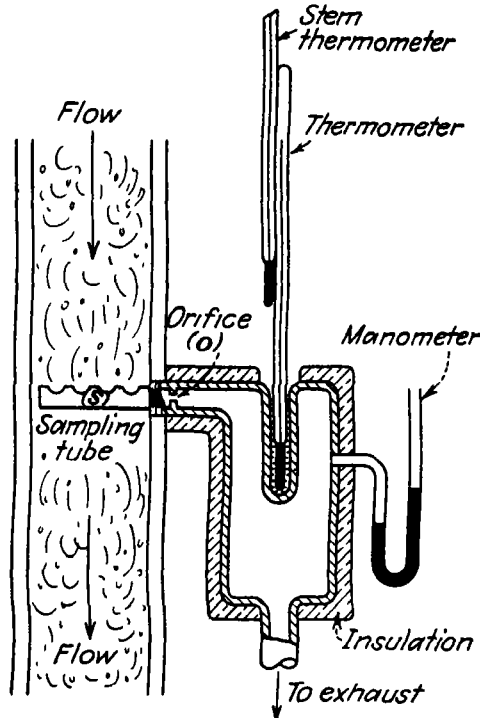


FIG. 6-7 Simple throttling calorimeter

**Example 11.** Steam under a pressure of 150 psia enters a throttling calorimeter and emerges as superheated steam at atmospheric pressure with a temperature of 300 F. What is the quality of the wet steam?

**Solution.** The state of the steam at the outlet from the calorimeter can be determined from Steam Table 3

$$\text{Measured } p_b = 14.696 \text{ psia (atmospheric pressure)}$$

$$t_b = 300 \text{ F}$$

From Steam Table 3

$$h_b = 1192.8 \text{ Btu/lb}_m$$

The initial state of the steam is defined by

$$p_b = 150 \text{ psia}$$

$$h_b = 1192.8 \text{ Btu/lb}_m$$

Steam Table 2 yields the saturated-liquid and -vapor values for 150 psia

$$h_f = 330.51 \text{ Btu/lb}_m$$

$$h_{fg} = 863.6 \text{ Btu/lb}_m$$

and

$$h_o = h_f + x h_{fg}$$

$$1192.8 = 330.51 + x(863.6)$$

$$x = 0.998, \text{ or } 99.8 \text{ per cent} \quad \text{Ans}$$

The steam in the two-phase region is essentially dry

The easier solution is to use the Mollier chart contained in the Steam Tables. On this chart the final conditions of pressure and temperature can be located in the vapor region (as in Fig. 6-6). Tracing a path of constant enthalpy from this point to the constant-pressure line of 150 psia locates the initial state in the two-phase region, and the quality can be directly read from the chart.

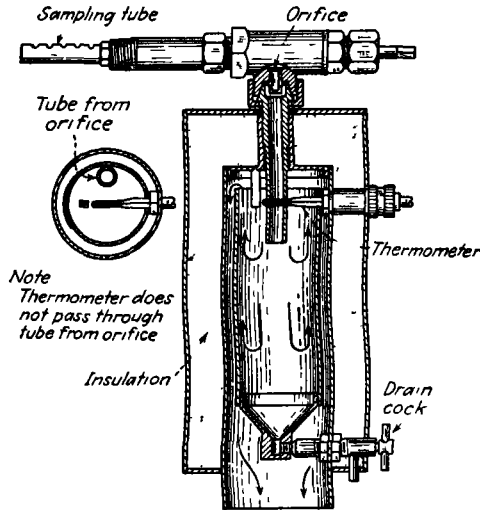


FIG. 6-8 Ellison throttling calorimeter (Ellison Draft Gauge Co.)

The calorimeter illustrated in Fig. 6-8 reduces heat loss to a minimum by leading the exhaust steam into a jacket around the inner container wherein temperature and pressure are measured. The outer shell of the calorimeter is filled with lampblack insulation to reduce heat losses from conduction and radiation further. The *normal correction* for this calorimeter is zero. The *normal correction* is the number of degrees of temperature that must be added to the observed calorimeter temperature to compensate for unavoidable heat loss. It is an empirical correction obtained by calibration of the calorimeter under conditions wherein the quality of the vapor is known.

Throttling calorimeters are limited in use since it is essential that the steam leaving the calorimeter be superheated. If the initial steam is too wet, this condition cannot be fulfilled. For accuracy it is desirable for the steam leaving the calorimeter to be at least  $5^{\circ}$  superheated, otherwise, misleading results may be obtained.

### Problems

1. Why do not the properties of pressure and specific volume define the state of a mixture at the triple point?
2. Explain the differences between the triple point and ice point.
3. For the traverse or cycle made in Fig. 6-1 list the proper name for each process.
4. Between states  $v$  and  $u$  in Fig. 6-1 the amount of saturated vapor increases from 0 to 100 per cent. Do the characteristics of this vapor change as the amount increases?
5. *a* If steam has a quality of 0.8 and pressure of 100 psia, find the specific values for volume, enthalpy, and entropy.  
*b* Repeat but use mercury as the fluid (Appendix, Table V).
6. One pound of steam at a pressure of 100 psia is confined in a closed tank with a volume of 4 ft<sup>3</sup>. Determine the quality, enthalpy, and entropy.
7. If the steam in Prob. 6 is to be heated until the temperature is 500 F, how much heat must be added?
8. If the steam in Prob. 6 is heated in a cylinder at constant pressure to 500 F, how much heat must be added?
9. Find the mean heat capacity of superheated steam at constant pressure from the saturated state at 150 psia to 500 F. Repeat, using range from 460 to 500 F.
10. *a* Saturated liquid at 100 F enters a pump and is reversibly compressed to 600 psia without transfer of heat. How much work is done by the pump?  
*b* If the pump is only 60 per cent as efficient as a reversible pump, how much work is done?  
*c* What is the enthalpy of the fluid leaving the irreversible pump?
11. If compressed water from the pumps of Prob. 10 enters a boiler where it is evaporated into dry saturated steam that leaves at a pressure of 600 psia, find the heat transferred for both cases.
12. Saturated water is isentropically compressed in a flow process from 100 F to a pressure of 800 psia. Find the work necessary for this process from Steam Table 4 and also by an approximate formula.  
*In the following problems, the work for compressing water can be determined by an approximate method.*
13. Feed water enters a steam boiler at 120 F while the steam leaves at 1,000 psia and 98 per cent quality. Find the heat transferred.
14. *a* A pound of saturated steam at 250 psia pressure is cooled at constant volume until its pressure falls to 100 psia. Determine the amount of heat transferred and the change in entropy.  
*b* Repeat, using carbon dioxide as the fluid (Appendix, Fig. III).
15. Three pounds of steam are processed in a closed and rigid container from

$p_1 = 14.7$  psia and  $T_1 = 300$  F to  $T_2 = 100$  F. Find  $p_2$ ,  $Q$ , and  $W$ , and sketch  $p$ - $v$  and  $T$ - $s$  diagrams for the change

16. Water, at the rate of  $1,000 \text{ lb}_m \text{ min}^{-1}$ , is to be heated from 60 to 200 F in a closed feed-water heater (water passes through coils surrounded by steam). The exhaust steam passing around the heater coil is initially at a pressure of 15 psia and contains 10 per cent moisture and leaves as saturated water

a How much steam is required per hour?

b What is the change in entropy for the steam and for the water?

c Sketch  $T$ - $s$  diagrams to illustrate the processes experienced by the liquid and the vapor

17. In the inlet pipe to an ideal turbine the steam is at a pressure of 150 psia and a temperature of 400 F. The exhaust is at 80 F while the rate of steam flow is  $1,200 \text{ lb}_m \text{ hr}^{-1}$

a Determine the work done per pound of steam.

b Calculate the horsepower developed

18. a Saturated steam at 150 psia enters a long pipe and leaves with a pressure of 144 psia. If no heat is lost by unavoidable radiation, etc., find the quality of the steam at exit

b If 10 Btu of heat are lost per pound of steam by radiation, etc., what will be the quality?

19. a Steam at 100 psia and 60 per cent quality receives  $350 \text{ Btu lb}_m^{-1}$  of heat while the pressure remains constant. Determine the resultant properties of the steam

b Repeat but use methyl chloride as the fluid and add only  $50 \text{ Btu lb}_m^{-1}$  of heat (Appendix, Fig. IV)

20. a A container with volume of  $10 \text{ ft}^3$  contains saturated steam at 100 psia. Determine the mass of steam within the tank

b Repeat but use methyl chloride as the fluid (Appendix, Fig. IV)

21. a Saturated steam at 100 psia enters a perfect turbine and expands isentropically to 5 psia. Find the work done by the turbine. Check the calculations using a Mollier chart

b Determine the final state of the steam if the work obtained from an adiabatic but irreversible expansion process is only 80 per cent of that determined in (a)

22. Repeat Prob. 21, assuming that the limits are 150 psia and 500 to 60 F

23. a Repeat Prob. 21, assuming that the limits are 100 psia (saturated) to 1 psia

b Repeat, using mercury as the fluid (Appendix, Table V)

24. a Saturated steam expands in a perfect nozzle from 150 psia to 40 F. Find the exit velocity if the initial velocity is negligible. Check the computations using a Mollier chart

b Repeat, using Freon F-12 as the fluid (Appendix, Table XVI)

25. Determine the heat that must be transferred to water initially at 60 F if the final temperature is to be 300 F and the process passes through a continuous series of saturated states (graphical solution as in Example 9)

26. a Steam at 100 psia and 96 per cent quality is throttled to atmospheric pressure. Find the temperature after throttling. Check the computation using a Mollier chart

b Repeat, using ammonia as the fluid (Appendix, Table XV)

27. Steam at 150 psia is throttled to atmospheric pressure with consequent

temperature of 230 F. What was the quality of the steam before the expansion? (Check computations using a Mollier diagram) If the normal correction is 5°, what will be the quality?

28. Repeat Prob 24 but assume that the initial pressure is 100 psia

29. Repeat Prob 27 but assume that the initial pressure is 50 psia

30. If saturated water at 150 psia were throttled to atmospheric pressure, what would be the final quality?

31. *a* Dry (saturated) steam at 100 psia enters a turbine and is throttled to 50 psia in the steam chest. Find the properties of the steam in the steam chest

*b* Repeat but use Freon F-12 as the fluid (Appendix, Table XVI)

32. The pressure in a steam calorimeter similar to that in Fig 6-8 is 4 in Hg above the atmospheric pressure. For steam initially at 100 psia, find the quality if the temperature in the calorimeter is 225 F

33. For conditions similar to those of Prob 32 the normal correction is 5 F while the flow of steam is 1 lb<sub>m</sub> sec<sup>-1</sup>. How much heat is lost per pound of steam by radiation, etc?

34. Steam at 150 psia and 500 F is isothermally and reversibly expanded in a cylinder until the pressure is 100 psia. Determine the work and heat transfers for this process of a closed system

35. *a* Steam at 150 psia and 500 F is expanded in a perfect nozzle to 3 psia. Find the final velocity if the initial velocity is 30 ft sec<sup>-1</sup>

*b* The high-velocity stream is slowed down in a perfect diffuser until the pressure is 100 psia. Determine the condition of the steam leaving the diffuser

36. Saturated steam at 180 psia and 30 ft sec<sup>-1</sup> velocity undergoes an irreversible but adiabatic steady-flow process to a pressure of 100 psia, quality of 90 per cent and final velocity of 10 ft sec<sup>-1</sup>. (*a*) Determine the work transferred and the change in entropy. (*b*) Repeat, using mercury as the fluid (Appendix, Table V)

37. Repeat Prob 36, but assume that the process is reversible and the final conditions are 100 psia and unknown quality

38. Air at 100 atm pressure and 350 R is isentropically expanded to 10 atm pressure. Find the change in enthalpy, the work that can be done, and the quality. (Use Fig II, Appendix)

39. *a* Air at 30 atmospheres pressure and 500 R expands in a throttling calorimeter to a pressure of 1 atmosphere. What will be the final temperature? (Use Fig II, Appendix)

*b* Repeat, using carbon dioxide as the fluid (Appendix, Fig III)

40. Steam at 53 psig and 300 F enters a steam-heating radiator in a room. The liquid leaving the radiator is saturated. Determine the steam required in pounds per hour if the heat exchange between the radiator and room is 15,000 Btu hr<sup>-1</sup>

41. Steam flows through a superheater at the rate of 1,000 lb<sub>m</sub> hr<sup>-1</sup>. At entrance to the heater  $p = 240$  psia,  $x = 100$  per cent, at exit from the heater  $p = 200$  psia and  $t = 480$  F. Determine the heat transferred, and show the process on  $pv$  and  $Ts$  diagrams

42. Steam flows through a nearly closed valve in a horizontal insulated pipe of 10 in inside diameter. Upstream from the valve the pressure is 400 psia, downstream the pressure is 50 psia and the temperature is 300 F. The flow rate is 697 lb<sub>m</sub> hr<sup>-1</sup>. Determine the transfers of heat and work, the initial temperature, and the change in entropy, and show process on  $pv$  and  $Ts$  diagrams

### Symbols

$c$	heat capacity
$F$	Fahrenheit scale
$f$	function
$G$	gas phase
$g_c$	dimensional constant for engineering system $\left(32\,1739\,\frac{\text{lb}_m\text{ft}}{\text{lb}_f\,\text{sec}^2}\right)$
$h$	enthalpy per unit mass (specific enthalpy)
$L$	liquid phase
$m$	mass, also, mass flow rate
$p$	pressure
$Q$	heat
$S$	solid phase
$s$	entropy per unit mass (specific entropy)
$t$	thermodynamic temperature
$T$	absolute thermodynamic temperature
$u$	internal energy per unit mass (specific internal energy)
$v$	specific volume
$V$	velocity
$W$	work
$x$	quality
$\approx$	closely equal

### Subscripts

$f$	force, saturated liquid
$fg$	change from saturated liquid to saturated vapor
$g$	saturated vapor
$isen$	isentropic
$m$	mass
$p$	constant pressure
$rev$	reversible
$x$	state where quality is $x$

### Suggested References

- 1 MATTHEWS, C S, and C O HURD Thermodynamic Properties of Methane, *Trans Am Inst Chem Eng*, **42** (No 1), 55-78 (Feb 25, 1946)
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- 3 NATIONAL BUREAU OF STANDARDS "Ammonia,"<sup>2</sup> Circular 142, April 16, 1923
- 4 WILLIAMS, V C Air at Low Temperatures,<sup>3</sup> *Trans Am Inst Chem Eng*, **39** (No 1), 93-111 (Feb 25, 1943)
- 5 QUINN, E L, and C L JONES "Carbon Dioxide,"<sup>4</sup> Reinhold Publishing Corporation, New York, 1936

<sup>1</sup> Discussed in Art 8-9

<sup>2</sup> Appendix, Table XV

<sup>3</sup> Appendix, Fig II

<sup>4</sup> See also Appendix, Fig III.









## CHAPTER VII

### CHARACTERISTICS OF GASES

Although thermodynamics does not need to inquire into the ultra-microscopic nature of a substance, the engineer can better understand the behavior of gases by considering the molecular activity. By so doing, a theoretical basis may be found for the  $p\nu T$  relationships of a gas, although the usual equations have been empirically modified to correspond more nearly to experimental data.

**7-1. The Idealized Gas.** A simple gas can be visualized as a space containing a number of molecules that have velocities ever changing because of collisions. Each molecule will consist of one or more atoms and contain or have associated with it a quantity of energy. This energy will be comprised of kinetic energy of translation of the molecule, of rotational and vibrational energy from motion of the atoms, and of potential energy arising from intermolecular forces. For there must exist forces of attraction or repulsion between the molecules, and these forces constitute a potential form of internal energy. All these types of internal energy bear a definite relationship to each other for each definite state of the gas. As the molecules move about in space, they collide with each other and interchange energy although the exact nature of the intermolecular collision can only be surmised. Whether or not a collision occurs will depend on the distance apart and the law of attraction between molecules. The gas can be made indefinitely rare to minimize the effects of such collisions, or near collisions, on the observed properties of the gas, and, by so doing, a limiting condition is approached by real gases where the behavior is unaffected by the presence of other molecules. Since all gases can approach this limit, it is considered to be an ideal or perfect state. In this perfect state the molecules behave as elastic spheres in a conservative mechanical system.

A *perfect* or *ideal* gas can be proposed as a standard of comparison for real gases. This idealized gas will exhibit two characteristics: (1) all force interactions between molecules will be absent; and (2) the aggregate size of all molecules will always be negligible in comparison with the size of the confining space. To satisfy the first condition, the

distribution of internal energy must be in forms entirely independent of the presence of other molecules of the perfect gas or, for that matter, of the presence of any other material body. To satisfy the second condition the size of the molecules of the perfect gas must approach zero, at least for conditions of high density.

**7-2. The Perfect Gas : Pressure.** When a molecule of perfect gas undergoes a collision, it behaves as a perfectly elastic sphere. Thus, when a molecule strikes the walls of the enclosing vessel, it rebounds without loss of velocity and exerts, for a brief instant, a force (impulse) on the wall. The continuous bombardment of the walls by the many molecules creates a constant pressure that is held in restraint by the vessel

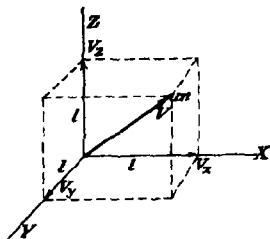


Fig 7-1 Vector velocities for a molecule in space

Consider a cube, with length of side  $l$ , that contains  $n'$  molecules of individual mass  $m$ . Suppose one of these molecules has a velocity  $V$  with components  $V_x$ ,  $V_y$ , and  $V_z$  in directions  $X$ ,  $Y$ , and  $Z$ , as illustrated in Fig 7-1. When this molecule strikes and rebounds from a wall of the cube, the component of velocity perpendicular to the wall is reversed in direction although the components in other directions

are not affected. Thus, the impulse force in the direction  $X$ , for example, is equal to the change in momentum, which is measured by the product of the mass and the change in  $V_x$ .

$$\text{Impulse per collision} = m(\Delta V_x) = 2mV_x$$

The molecule will cross the cube and return in the time  $2l/V_x$ , hence, in 1 sec it will impinge on one wall of the container.

$$\text{Collisions per second} = \frac{V_x}{2l}$$

The force exerted on one wall of the container by one molecule is

$$\begin{aligned} F_x &= (2mV_x) \frac{V_x}{2l} \\ &= m \frac{V_x^2}{l} \end{aligned}$$

And for  $n'$  molecules with various velocities

$$F_x = \frac{m}{l} \sum V_x^2$$

Let  $(V_x^2)_{\text{avg}}$  be the average value of the squares of the velocities in the  $X$  direction for  $n'$  molecules

$$F_x = \frac{mn'(V_x^2)_{\text{avg}}}{l}$$

For stability, the same force must be exerted on each wall of the cube

$$F_x = F_y = F_z$$

Therefore,

$$(V_x^2)_{\text{avg}} = (V_y^2)_{\text{avg}} = (V_z^2)_{\text{avg}}$$

This relationship and Fig 7-1 show

$$(V^2)_{\text{avg}} = (V_x^2)_{\text{avg}} + (V_y^2)_{\text{avg}} + (V_z^2)_{\text{avg}} = 3(V_x^2)_{\text{avg}} = 3(V_y^2)_{\text{avg}} = 3(V_z^2)_{\text{avg}}$$

Hence,

$$F = \frac{mn'}{3l} (V^2)_{\text{avg}}$$

The pressure is found by dividing the force by the area

$$p = \frac{F}{l^2} = \frac{mn'}{3l^3} (V^2)_{\text{avg}}$$

and, for  $n$  molecules per unit volume ( $n = n'/l^3$ ),

$$p = \frac{1}{3}mn(V^2)_{\text{avg}} \quad (a)$$

The product  $mn$  is, by definition, the density or mass per unit volume

$$\begin{aligned} p &= \frac{1}{3}\rho(V^2)_{\text{avg}} \\ pv &= \frac{1}{3}(V^2)_{\text{avg}} \end{aligned} \quad (b)$$

Suppose that two different gases are present in a mixture. The molecules will differ from each other only in size and velocity. The total pressure from the two gases will be the sum of the impacts from all of the molecules. The same procedure as above can be used to sum up all momentum changes, which will be

$$p = \frac{n_a m_a}{3} (V_a^2)_{\text{avg}} + \frac{n_b m_b}{3} (V_b^2)_{\text{avg}} \quad (c)$$

or

$$p_{\text{total}} = \Sigma \text{ partial pressure of each component} = p_a + p_b \quad (d)$$

A statement of the above equation is known as *Dalton's law*, and it is approximately true for real gases

**The pressure of a mixture of perfect gases is equal to the sum of the partial pressures which the component gases would exert**

if each existed alone in the mixture volume at the mixture temperature.

**7-3. The Perfect Gas: Temperature.** If a cold thermometer is inserted into a gas, the impact of the molecules will transfer energy to the molecules of the thermometer. If the thermometer is hotter than the gas, the molecules striking the thermometer will rebound with a greater velocity than before the impact. However, when the thermometer and gas have the same temperature, no net exchange of energy will occur. How soon this equilibrium of temperature will be reached depends on the number of molecules striking the thermometer, that is, upon the density of the gas. The same temperature level will be shown no matter how low or how high the density varies as long as the average kinetic energy of the impacts remains constant. Similarly, if the temperature of some other gas is measured, the same temperature will be recorded when the average kinetic energies of both gases are the same. Consequently, for equality of temperature between two gases  $a$  and  $b$ ,

$$\frac{1}{2}m_a(V_a^2)_{\text{avg}} = \frac{1}{2}m_b(V_b^2)_{\text{avg}} \quad (e)$$

Equation (c) was for a mixture of perfect gases and can have but one temperature. Substituting Eq (e) in Eq (c),

$$p = \frac{1}{3}m_{(a \text{ or } b)}(V_{a \text{ or } b}^2)_{\text{avg}}(n_a + n_b)$$

Comparison with Eq (d),

$$p = p_a + p_b$$

shows that the partial pressure of a perfect gas depends on the number of molecules of that gas present in the mixture. If both partial pressures are equal, then  $n_a = n_b$ . This result is known as *Avogadro's hypothesis*:

**Equal volumes of perfect gases under the same conditions of temperature and pressure contain equal numbers of molecules.**

It necessarily follows that the densities of perfect gases at the same temperature and pressure must bear the same relationship to each other as their molecular weights  $M$ , or

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2} \quad (7-1a)$$

and

$$\frac{v_2}{v_1} = \frac{M_1}{M_2} \quad (7-1b)$$

Consider a perfect gas confined in chamber *A* of Fig. 7-2. If the partition is removed, the gas will expand and fill the evacuated chamber *B* (Joule's expansion, Art 3-2). The specific volume increases while the density correspondingly decreases and the pressure, of course, decreases. Nothing in this operation will change the average translational velocity of the molecules unless an attraction between the molecules exists. Because no such attraction exists for the perfect gas, the kinetic energy must remain constant and, therefore, the temperature will remain constant.

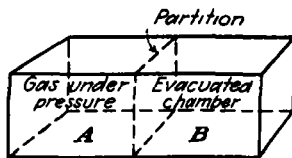


FIG 7-2. Joule's free expansion

$$\begin{aligned}
 p_1 v_1 &= p_2 v_2 = \frac{1}{3}(V^2)_{\text{avg}} \\
 p_1 v_1 &= p_2 v_2 = C \Big|_{t=c} \\
 \left. \frac{p_1}{p_2} = \frac{v_2}{v_1} \right]_{t=c}
 \end{aligned} \tag{f}$$

This result is known as *Boyle's law*.

**The pressure and specific<sup>1</sup> volume of a perfect gas are inversely proportional to each other under conditions of constant temperature.**

The free-expansion process was not only at constant temperature but also at constant internal energy, and this result is known as *Joule's law*.

**The internal energy of a perfect gas is a function only of temperature.**

**7-4. The Perfect Gas : The Thermodynamic Temperature.** As the temperature of the perfect gas is increased, the velocity of the molecules is also increased, and therefore the value of the  $pv$  product will progressively increase with temperature. Hence, in the Boyle equation, the product  $pv$  for each gas can have only one value at each temperature, and this value of  $pv$  is, in itself, a temperature. It will be shown that the  $pv$  product differs only by a constant factor from the Carnot thermodynamic temperature.

Consider the cycle of an ideal gas, illustrated in Fig 7-3, that consists of two isothermal and two constant-volume processes. Joule's law shows that the decrease in temperature and internal energy during

<sup>1</sup> Or if the mass and the temperature are held constant, the pressure and volume are inversely proportional to each other.



process 1-2 is exactly equal to the increase in temperature and internal energy during process 3-4. Because of this fact, such a cycle can be *regenerated*. To do this regeneration an infinite number of reservoirs, each at a definite temperature, can be used to store the energy removed during process 1-2. Later in the cycle, these same reservoirs can be used to supply the equivalent amount of energy necessary for process 3-4. The net effect of the regeneration is that heat is transferred to the system of cycle and reservoirs only at a constant temperature  $T_1$  during process 4-1 and, similarly, heat is rejected by the system only at a constant temperature  $T_2$  during process 2-3.

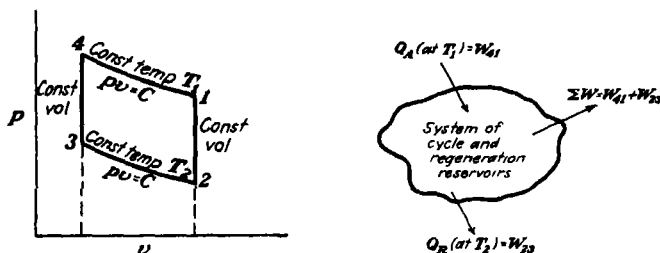


FIG. 7-3. Regenerative cycle equivalent in thermal efficiency to the Carnot cycle.

The heat added to the cycle from an external reservoir equals the work done during the isothermal process 4-1

$$Q - W = \Delta u = 0 \quad (\text{Joule's law})$$

and

$$W = \int p dv$$

where

$$pv = \text{constant} \quad (\text{Boyle's law})$$

Hence,

$$Q_A = W_{4-1} = C \int \frac{dv}{v} = p_1 v_1 \ln \frac{v_1}{v_4}$$

In the same manner the work for the isothermal process 2-3 and, therefore, the heat rejected by the cycle are

$$Q_R = W_{2-3} = p_2 v_2 \ln \frac{v_3}{v_2}$$

The ratio of the heat rejected to the heat added is

$$\frac{Q_R}{Q_A} = \frac{p_2 v_2 \ln v_3/v_2}{p_1 v_1 \ln v_1/v_4}$$

But, from Fig. 7-3,

$$v_2 = v_1$$

$$v_3 = v_4$$

Hence,

$$\frac{-Q_R}{Q_A} = \frac{p_2 v_2}{p_1 v_1} \quad (g)$$

Since in this regenerative cycle heat is added and rejected only at constant temperatures, and since all processes are reversible, then the thermal efficiency of the cycle must be equal to that of the Carnot cycle (Art 5-3) Equation (5-1a) shows that

$$\frac{-Q_R}{Q_A} = \frac{T_2}{T_1} \quad (5-1a)$$

If Eqs (g) and (5-1a) are combined,

$$\frac{-Q_R}{Q_A} = \frac{p_2 v_2}{p_1 v_1} = \frac{T_2}{T_1}$$

resulting in

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad (7-2)$$

This is the relationship between the product  $pv$  for the perfect gas and the Carnot thermodynamic temperature

Equation (7-2) offers a practical method for determining temperatures on the absolute thermodynamic scale Hydrogen or helium, either of which can behave like a perfect gas, is used in either a constant-pressure or a constant-volume gas thermometer A constant-volume gas thermometer, as its name implies, consists of a constant-volume reservoir for the gas and apparatus to measure the pressure. For such a thermometer, Eq (7-2) can be applied to measurements made at the ice and steam points:

$$\frac{T_2}{T_1} = \frac{p_2 v_2}{p_1 v_1}$$

$$\frac{z + 212 \text{ F}}{z + 32 \text{ F}} = \frac{p_2}{p_1} = 1.366 \quad (\text{a value found by test})$$

$$z = 459.69 \text{ F}$$

Measurements show this ratio to be 1.366, and, therefore, the absolute thermodynamic temperatures can be calculated for these two reference points

**7-5. The Perfect Gas: Equation of State.** Equation (7-2) can be directly converted into an *equation of state*:

$$\frac{p_2 v_2}{p_1 v_1} = \frac{T_2}{T_1}$$

or

$$pv = RT \quad (7-3a)$$

where  $R$  is a dimensional constant that is a characteristic of the gas. Since

$$v = \frac{\text{volume}}{\text{mass}} = \frac{V}{m}$$

then,

$$pV = mRT \quad (7-3b)$$

In this equation of state, the value of  $R$  will be different for each gas. However, a *universal* gas constant can be found from Avogadro's law. Consider two gases with identical conditions of pressure, temperature, and volume:

$$\frac{v_a}{v_b} = \frac{M_b}{M_a} \quad (7-1b)$$

But, from Eq (7-3a),

$$\frac{v_a}{v_b} = \frac{R_a T / p}{R_b T / p} = \frac{R_a}{R_b}$$

and therefore

$$\frac{v_a}{v_b} = \frac{M_b}{M_a} = \frac{R_a}{R_b} \\ R_a M_a = R_b M_b = R_0 \quad (7-4)$$

where  $R_0$  is a *universal gas constant*. [Values for  $R_0$  have been experimentally determined by tests on real gases at low pressures to simulate ideal-gas conditions (Table IV, Appendix) ] If this universal constant is used in Eq (7-3b) obviously it will be too large because of the multiplying factor  $M$ . This difficulty can be avoided by dividing the mass of gas by the same factor:

$$pV = \frac{m}{M_a} (R_a M_a) T \\ pV = n R_0 T \quad (7-5)$$

When this is done, a new unit of mass, designated by the letter  $n$ , is defined—the *mole*

$$n = \frac{m}{M} \quad (7-6)$$

The mole is defined as a mass of material, of amount equal to the molecular weight. For example, a pound mole of oxygen has a mass of 32.0 pounds; a pound mole of carbon dioxide has a mass of 44 pounds. Although the mole is a unit of mass, it should be remembered that the mole cannot be expressed in terms of other mass units unless the molecular weight is known. The mole in any units will be designated by the letter  $n$ . A pound mole will be designated by the abbreviation *mole*, while for other mass units a prefix will be used, as, for example, *g-mole* for the gram mole.

The mole is a peculiar mass unit in that 1 mole will have different amounts of mass for different fluids. The mole is a mass unit that contains the same number of molecules of one fluid as does a mole of any other fluid. The mole unit is not restricted to perfect gases but may be used for solids, liquids, or gases. For perfect gases the mole can be considered to be a unit of volume. For by Eq. (7-5),

$$V = \frac{nR_0T}{p}$$

and the volume of 1 mole of any perfect gas under the same conditions of pressure and temperature must be a constant.

Although the universal gas constant is here distinguished from the specific gas constant by a subscript, in the following pages the subscript will not always be used. For by Eq. (7-3a)

$$pv = RT$$

and the specific volume  $v$  has units of

$$v = \frac{\text{volume}}{\text{mass}}$$

If the mass unit is the pound (or gram), then  $R$  must be the *specific* gas constant, if the mass unit is the mole, then  $R$  must be the *universal* gas constant.

**Example 1:** Determine the dimensions and engineering units for  $R$  in Eqs (7-3b) and (7-5).

**Solution:**

$$[R] = \left[ \frac{pV}{mT} \right] = \left[ \frac{FL^3}{L^2MT} \right] = \left[ \frac{FL}{MT} \right] \quad (7-3b)$$

$$\text{Engineering units} = \frac{\text{lb}_f \text{ ft}}{\text{lb}_m \text{ R}} \text{ or } \frac{\text{lb}_f \text{ in}}{\text{lb}_m \text{ R}}$$

$$[R] = \left[ \frac{pV}{nT} \right] = \left[ \frac{FL^3}{L^2MT} \right] = \left[ \frac{FL}{MT} \right] \quad (7-5)$$

$$\text{Engineering units} = \frac{\text{lb}_f \text{ ft}}{\text{mole R}} \text{ or } \frac{\text{lb}_f \text{ in}}{\text{mole R}}$$

This example shows that no subscript is necessary to designate the two gas constants because both have the same dimensions (and the same reasoning shows that a new symbol  $n$  for the mole unit is illogical) Note that  $R$  can also be expressed in thermal units (Table IV, Appendix)

**Example 2:**

$$\text{Convert } 1,545 \frac{\text{ft lb}_f}{R \text{ mole}} \text{ to } \frac{\text{atm ft}^3}{\text{mole } R}$$

**Solution:** From Table I (Appendix)

$$1 \text{ atm} = 2,120 \frac{\text{lb}_f}{\text{ft}^2}, \text{ or } 2,120 \frac{\text{lb}_f}{\text{atm ft}^2}$$

and therefore

$$1,545 \frac{\text{ft lb}_f}{R \text{ mole}} \frac{\text{atm ft}^2}{2,120 \text{ lb}_f} = 0.730 \frac{\text{atm ft}^3}{R \text{ mole}} \quad \text{Ans}$$

**Example 3:** (a) Determine the volume of 1 mole of air at standard conditions of  $p = 14.7$  psi and  $t = 60$  F. (b) What is the mass of this volume?

**Solution:**

a From Eq (7-3a) (value for  $R_0$  from Table IV, Appendix)

$$\begin{aligned} v &= \frac{R_0 T}{p} & R_0 &= 10.73 \frac{\text{psia ft}^3}{\text{mole } R} \\ &= \frac{(10.73)(520)}{14.7} \\ &= 380 \text{ ft}^3/\text{mole} \quad \text{Ans} \end{aligned}$$

Whether or not this is the true answer will depend on how closely air is truly represented by Eq (7-3a)

b The mass is 1 mole or 28.96 lb<sub>m</sub> (Table VI, Appendix) Ans

**Example 4:** Determine the density of nitrogen in engineering units at conditions of  $p = 20$  psi and  $t = 100$  F if the gas is considered perfect

**Solution:** The molecular weight of nitrogen is 28 (Table VI, Appendix) From Eq (7-3a)

$$\begin{aligned} pv &= RT \\ \rho &= \frac{1}{v} = \frac{p}{RT} \\ \rho &= \frac{20}{\left(\frac{10.73}{28}\right)(560)} \\ &= 0.0934 \text{ lb}_m/\text{ft}^3 \quad \text{Ans} \end{aligned}$$

**7-6. The Perfect Gas: Internal Energy and Heat Capacity.** The simplest perfect gas would have monatomic molecules. For such a gas the internal energy would be entirely energy of translation. Then, from Eq (b) in Art. 7-2,

$$pv = \frac{1}{3}(V^2)_{\text{ave}}$$

Also,

$$pv = RT \quad (7-3a)$$

and for unit mass<sup>1</sup>

$$\frac{1}{2}(V^2)_{\text{ave}} = RT \quad (h)$$

The kinetic energy for unit mass is  $\frac{1}{2}(V^2)_{\text{ave}}$  and this form of energy was assumed to be the entire internal energy or

$$u = \text{KE} = \frac{1}{2}(V^2)_{\text{ave}}$$

By Eq (h)

$$u = \frac{3}{2}RT \quad (i)$$

and this is the value of internal energy for the monatomic gas. The enthalpy is defined

$$h = u + pv \quad (2-6a)$$

When Eq (i) and (7-3a) are substituted,

$$\begin{aligned} h &= \frac{3}{2}RT + RT \\ h &= \frac{5}{2}RT \end{aligned} \quad (j)$$

and this is the value of enthalpy for the monatomic gas

The heat capacities at constant volume and constant pressure have been defined (Art 4-7) as

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v \quad c_p = \left( \frac{\partial h}{\partial T} \right)_p$$

For the perfect gas,  $u$  and  $h$  are properties dependent only upon temperature and can therefore be evaluated without regard to pressure or volume

$$c_v = \frac{du}{dT} \quad c_p = \frac{dh}{dT}$$

When the values for  $u$  and  $h$  given by Eqs (i) and (j) are substituted, it is evident that

$$c_v = \frac{3}{2}R \quad c_p = \frac{5}{2}R \quad c_p - c_v = R$$

Thus, the heat capacities are found to be constants—a result that could have been foreseen from the initial assumption that a change in internal energy is directly proportional to the translational energy. The difference between  $c_p$  and  $c_v$  is always a constant for the perfect gas whether or not the heat capacities are constant

$$\begin{aligned} c_p - c_v &= \frac{dh}{dT} - \frac{du}{dT} = \frac{du + RdT}{dT} - \frac{du}{dT} \\ c_p - c_v &= R \end{aligned}$$

<sup>1</sup> Since  $R$  is commonly expressed in either mechanical or thermal units (Table IV, Appendix), equations involving  $R$  need not contain the conversion factor  $J$

Another relationship that will be valuable in later work is the ratio of  $c_p$  to  $c_v$ . This ratio is designated by the letter  $k$ , and for monatomic perfect gases

$$k = \frac{c_p}{c_v} = \frac{5/2}{3/2} = \frac{5}{3} = 1.666$$

A famous theorem of classical mechanics, called the *equipartition of energy*, states that, when each part of the energy of a system is proportional to the square of a coordinate, then all such parts must be equal. This theorem can be illustrated by the monatomic molecule that has a velocity component in three directions,  $x$ ,  $y$ , and  $z$  (Fig. 7-1). Since there are three degrees of translational freedom, the total kinetic energy is made up of three equal parts and each part can be assigned a value  $\frac{1}{2}R$  by Eq. (2).

The internal energy of complex molecules is distributed over degrees of freedom that are mainly associated with translational, rotational, and vibrational energies. Although translational energy can continuously vary in value, all other forms of internal energy are restricted to a series of energy levels. For example, consider a gas with molecules of two atoms arranged like a dumbbell. At any temperature a certain percentage of the molecules will have a definite energy level although transitions into and out of such states are continuous. At extremely low temperatures, the number of molecules possessing rotational energy will be small, and still smaller will be the number with vibrational energy. Consequently, the average internal energy and average heat capacity for the gas will approach the values for the monatomic gas because the internal energy will consist mainly of translational kinetic energy. As the temperature is raised, however, more and more of the molecules are activated to a higher energy level with attendant rotation of the dumbbell molecule about two axes perpendicular to the axis of symmetry (two degrees of rotational freedom). If it is assumed that most of the molecules are in this state and that the internal energy is equally divided among the five degrees of freedom (three translational and two rotational), then for this perfect gas,

$$c_p = \frac{7}{2}R \quad c_v = \frac{5}{2}R \quad c_p - c_v = R \quad k = \frac{c_p}{c_v} = 1.4$$

However, a fraction of the molecules are in the lower energy levels of no rotation, and another fraction are in the higher energy level of vibration. For this latter condition the two atoms of the molecule can be considered to have a vibratory motion along the axis of the molecule. If the temperature again is raised, a state can be attained where

most of the molecules possess translational, rotational, and vibrational energy. The additional degrees of freedom are two, and, assuming the equipartition of energy,

$$c_p = \frac{9}{2}R \quad c_v = \frac{7}{2}R \quad c_p - c_v = R \quad k = \frac{c_p}{c_v} = 1.286$$

For a three-atom rigid molecule there could be three degrees of rotational and three degrees of translational freedom

$$c_p = \frac{8}{2}R \quad c_v = \frac{6}{2}R \quad c_p - c_v = R \quad k = \frac{c_p}{c_v} = 1.33$$

These would be the classical values of the heat capacities for triatomic molecules at temperatures such that rotational energies were excited (but not vibrational energies) for all of the molecules.

Although for the individual molecule the transition from one state of excitation to another state is abrupt, it should be remembered that a gas consists of a tremendous number of molecules. The variation of heat capacity with temperature for a finite amount of gas is a smooth curve because the discontinuities of the individual molecule are a negligible part of the total variation.

For the perfect gas, no assumption need be made as to the type of molecule. Thus, in the general case the heat capacities of the perfect gas will increase with temperature but will be independent of pressure or volume.

It is evident from the above discussion that for the perfect gas

$$du = c_v dT \quad (7-7)$$

$$dh = c_p dT \quad (7-8)$$

$$c_p - c_v = R \quad (7-9)$$

and, by definition,

$$k = \frac{c_p}{c_v} \quad (7-10)$$

where  $c_p$  and  $c_v$  can be constants or quite involved functions of temperature. From these last two equations it is easily shown that

$$c_p = \frac{kR}{k-1} \quad (7-11)$$

$$c_v = \frac{R}{k-1} \quad (7-12)$$

All the above values are based upon the perfect-gas criterion of zero potential internal energy arising from a force field around the



molecule. Such values can be approached by the real gas only at greatly reduced densities where the potential-energy effects, which the real molecule experiences, are minimized. Thus,  $c_v = \frac{3}{2}R$  is the limiting value for all gases as the temperature approaches absolute zero.<sup>1</sup> The heat capacities of the real monatomic gases are not affected by temperature because rotational and vibrational energies are absent for such simple molecules. For real gases with more than one atom as the temperature is raised, more and more molecules enter a state wherein

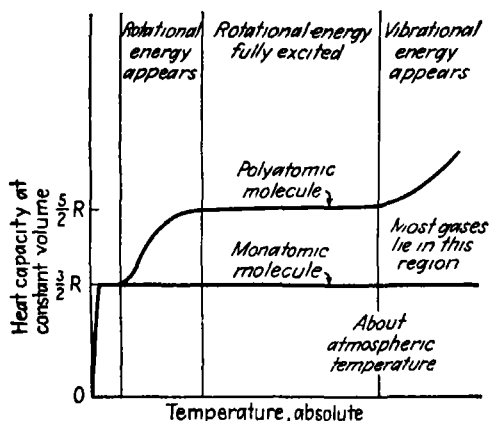


Fig 7-4 The effect of temperature on the  $c_v$  of gases

both translational and rotational energies are present, this transition occurs at low temperatures. As the temperature is raised still higher, vibrational energy of the atomic nucleus will appear at about atmospheric temperature for most gases. Because of these changes the heat capacities of real gases with more than one atom in the molecule increase with temperature for the same reasons as for a perfect gas. This variation is illustrated in Fig 7-4. However, for the real gas the effect of pressure on the heat capacity may be considerable (Fig I, Appendix). The difference between the heat capacities at constant pressure and constant volume for real gases is never less than  $R$  but may be much greater because of pressure.

Spectroscopic measurements on gases used in connection with relationships derived from quantum mechanics have made possible the accurate calculation of heat capacities at high temperatures (Table IIB, Appendix). The spectroscopic data as obtained are for gases at zero pressure, that is, with no molecular interaction in the gas. This condition of zero pressure is highly unreal for engineering application,

<sup>1</sup> But at absolute zero the heat capacity becomes zero

but it happens that for many cases the values at zero pressure can be used with little error (refer to Fig I, Appendix). For temperatures above 1000 F and pressures not exceeding 500 psi, the zero pressure values for the constant-pressure heat capacities in general are less than 2 per cent low and may be used without correction. The deviation becomes less as the temperature rises. Carbon dioxide, among the

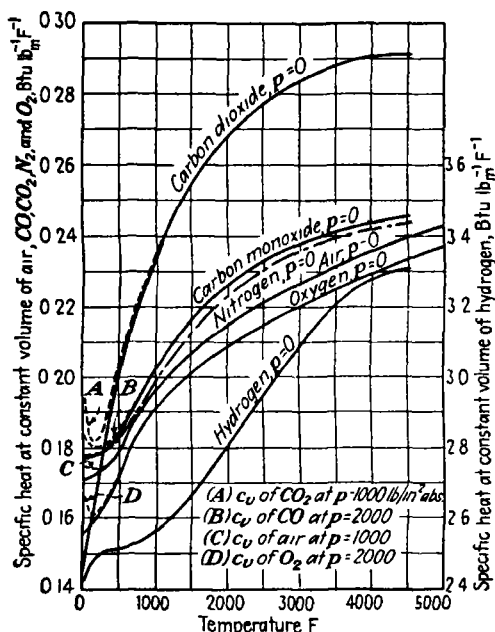


FIG 7-5 The effects of temperature and pressure on the  $c_v$  of real gases (from Reference 4)

common gases, evidences a rather large variation. At 1000 F and 500 psi the true value for  $c_p$  is only 2 per cent higher than the zero pressure value; at 100 F and 500 psi the correct value is 14 per cent higher than the zero pressure value. The heat capacity at constant volume is affected even less by pressure, as illustrated in Fig 7-5

**Example 5:** Determine the average heat capacity at constant pressure for nitrogen between temperatures of 1000 and 2000 R

**Solution:** From Table IIB (Appendix) for nitrogen,

$$c_p = 9.47 - \frac{3.47(10^3)}{T} + \frac{1.16(10^6)}{T^2}$$

$$c_p = \frac{\int_{1000}^{2000} \left[ 9.47 - \frac{3.47(10^3)}{T} + \frac{1.16(10^6)}{T^2} \right] dT}{2000 - 1000}$$

$$\begin{aligned}
 &= \frac{9.47(T_2 - T_1) - 3.47(10^3) \ln \frac{T_2}{T_1} - 1.16(10^6) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}{1000} \\
 &= 9.47 - 2.41 + 0.58 \\
 &= 7.64 \text{ Btu/mole R} \quad \text{Ans}
 \end{aligned}$$

A solution can also be found from the data in Table IIC (Appendix). Thus, the mean molal heat capacity for nitrogen between 32 and 1540 F is

$$c_{pm} = 7.381 \text{ Btu/mole R} \quad (\text{Table IIC})$$

and between 32 and 540 F is

$$c_{pm} = 7.034 \text{ Btu/mole R} \quad (\text{Table IIC})$$

Since

$$\int_{540 \text{ F}}^{1540 \text{ F}} c_p dT = \int_{32 \text{ F}}^{1540 \text{ F}} c_p dT - \int_{32 \text{ F}}^{540 \text{ F}} c_p dT$$

then,

$$\int_{540 \text{ F}}^{1540 \text{ F}} c_p dT = 7.381(1540 - 32) - 7.034(540 - 32) = 7535$$

and

$$c_{pm} \int_{540 \text{ F}}^{1540 \text{ F}} dT = \frac{\int_{540 \text{ F}}^{1540 \text{ F}} c_p dT}{1540 - 540} = 7.535 \text{ Btu/mole R} \quad \text{Ans}$$

This answer differs from that found in the first solution because the data of Table IIC are older and therefore probably less precise than the more recent equations in Table IIB. Table IIC was included to illustrate a method of presenting mean values of the heat capacities.

**7-7. The van der Waals' Equation.** It was assumed for the perfect gas that the length of path between collisions with the walls was not changed by the presence of other molecules. Actually, as more and more molecules are present in a volume (as the density is increased), the number of times a molecule will strike the walls will be increased and a greater pressure will be exerted than that predicted by the simple theory. In the year 1873 van der Waals premised that the increased pressure would be inversely proportional to the actual volume, that is, to the free space when allowance is made for the finite size and number of molecules

$$\begin{aligned}
 \frac{p_{\text{perfect}}}{p_{\text{actual}}} &= \frac{\text{actual volume}}{\text{total volume}} = \frac{v - b}{v} \\
 p_{\text{perfect}} &= p \left( \frac{v - b}{v} \right)
 \end{aligned}$$

But, also,

$$p_{\text{perfect}} = \frac{RT}{v}$$

and therefore

$$p = \frac{RT}{v - b}$$

where  $b$  is a constant for each gas

The second basic assumption for the perfect gas was that the molecules were neither attracted nor repulsed by the other molecules present. In the real gas a force field exists around the molecule. As the density increases, the molecules approach closer to each other and exert an increasing cohesive force of attraction until, in the limit, the molecules cling together to form the liquid phase. The pressure that a gas can exert is less than some ideal value by an amount equal to the restraining pull of the other molecules. Van der Waals assumed this decrease or potential energy to be proportional to the square of the density. He proposed adding a factor  $a/v^2$  to the kinetic pressure to account for this restraint. The final corrected equation of van der Waals is

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v - b} \quad (7-13a)$$

Here  $a$  and  $b$  are constants for the particular gas. This can be written

Total pressure = kinetic pressure - potential pressure

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (7-13b)$$

$$RT = \left(p + \frac{a}{v^2}\right)(v - b) \quad (7-13c)$$

The calculation of temperature or of pressure can be readily made from the van der Waals' equation, but calculations of specific volume must be made by successive approximations. For this reason the equation is said to be *explicit* only for temperature and pressure.

The corrections that are made by the constants  $a$  and  $b$  can be more clearly understood by examining Eq. (7-13b). Note that the two terms, one containing  $a$  and the other  $b$ , on the right-hand side of the equation oppose each other in effect. Since  $b$  corrects the equation for the finite size of the molecules, the value of  $b$  must be of the same order of magnitude as the volume of the liquefied gas. For this reason the effect of  $b$  to increase the pressure predicted by van der Waals' equation is small at low and medium pressures where the value of specific volume is large. However, at high pressures the specific volume is small, and  $b$  will exert a strong influence on the pressure dictated by the equation. The term  $a/v^2$  corrects the equation for the potential

attraction between the molecules, and this attraction is present at all pressures above zero but becomes more pronounced at high densities. Hence, the term  $a/v^2$  continually increases in value as the specific volume decreases, although the effect of the term on the pressure is quite evident even at low and medium pressures.

Note from Eqs (7-13) that the dimensions of  $a$  must be  $[FL^4/M^2]$ , and for  $b$ ,  $[L^3/M]$ . Values of  $a$  and  $b$  for several gases can be found in Table VIII (Appendix).

**Example 6:** Compute, using van der Waals' equation, the pressure exerted by 1 lb<sub>m</sub> of CO<sub>2</sub> at a temperature of 212 F if the specific volume is 0.193 ft<sup>3</sup>/lb<sub>m</sub><sup>1</sup>.

**Solution:** Since Table VIII (Appendix) is in mole units, it will be easier to convert the specific volume to a mole basis (or change the constants in Table VIII by use of the factors listed in this table). Then,

$$\begin{aligned} \text{Table IV} \\ M &= 0.73 \frac{\text{atm ft}^3}{\text{R mole}} \\ v &= 0.193(44) \\ &= 8.492 \text{ ft}^3/\text{mole} \\ T &= 672 \text{ R} \end{aligned}$$

$$\begin{aligned} \text{Equation (7-13b)} \\ p &= \frac{RT}{v-b} - \frac{a}{v^2} \\ &= \frac{0.73(672)}{(8.492 - 0.685)} - \frac{924.2}{(8.492)^2} \\ &= 62.9 - 12.8 \\ &= 50.1 \text{ atm} \end{aligned}$$

$$\begin{aligned} \text{Table VI} \\ M_{\text{CO}_2} &= 44 \end{aligned}$$

$$\begin{aligned} \text{Table VIII} \\ a &= 924.2 \frac{\text{atm ft}^6}{\text{mole}^2} \\ b &= 0.685 \text{ ft}^3/\text{mole} \end{aligned}$$

$$\begin{aligned} \text{Equation (7-3a)} \\ p &= \frac{RT}{v} = \frac{0.73(672)}{8.492} \end{aligned}$$

$$p = 57.8 \text{ atm} \quad \text{Ans}$$

Compare these two answers. Which answer is correct can be determined only by experiment, although the van der Waals' answer should be, and usually is, more reliable.

**7-8. Van der Waals' Isothermals and the Critical Point.** If the pressure is plotted against specific volume for conditions of constant temperature, van der Waals' equation will yield an odd series of curves (Fig 7-6) called van der Waals' isothermals. At high temperatures the curve approaches the hyperbolic curve for the simple gas because only one real root will be found for specific volume in solving Eqs (7-13). However, since Eqs (7-13) are cubic in  $v$ , three roots are possible, and at low temperatures all these roots are real. Van der Waals' isothermals in this region exhibit a rising and falling characteristic *defg* (Fig 7-6). An explanation for such behavior is apparent; since the equation has terms to correct for the effect of the size of the molecules, these terms become significant in the region of increased density, which corresponds to the two-phase region of Fig 6-3. A typical two-phase region is shown by the dashed curve in Fig 7-6 terminating at  $c$ , the critical point, where the slope of the isothermal is

zero. Obviously, van der Waals' equation cannot be used in the two-phase region since actually the pressure remains constant along an isothermal, but it is interesting to observe that the path of the equation approaches that of the real fluid. Note that, as the specific volume approaches  $b$ , the pressure predicted by Eqs (7-13) becomes infinite.

The critical point, however, is of particular interest. Here the tangent to the isotherm is horizontal at a point of inflection. At a

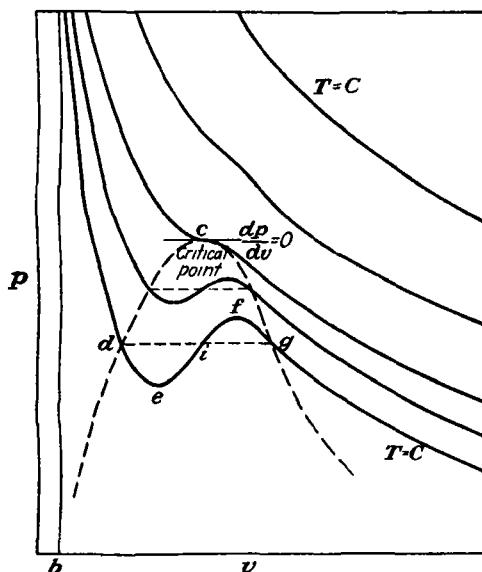


FIG 7-6 The van der Waals' isothermals

point of inflection, the curve changes from concave upward to concave downward as at  $c$  and also at  $t$  and thus the tangent reverses the sense in which it turns. This means that the derivative changes from an increasing to a decreasing function, or vice versa, and this requires the second derivative to become zero and change sign. The first derivative when set equal to zero will locate points where the tangent becomes horizontal—such as the critical point at  $c$ , the maximum at  $f$ , and the minimum at  $e$ . The second derivative when set equal to zero will locate points of inflection such as those at  $c$  and  $t$ . Then, to locate the critical point, it will be necessary to find only the value for  $v$  that will satisfy both equations

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \quad (7-14)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 \quad (7-15)$$

For the van der Waals' equation,

$$\begin{aligned} \left(\frac{\partial p}{\partial v}\right)_T &= \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \\ \left(\frac{\partial^2 p}{\partial v^2}\right)_T &= \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \end{aligned}$$

When these are solved simultaneously,

$$v_c = 3b \quad (7-16a)$$

$$T_c = \frac{8a}{27bR} \quad (7-16b)$$

On substituting these values in Eqs (7-13) and solving for  $p$ ,

$$p_c = \frac{a}{27b^2} \quad (7-16c)$$

From these equations and measured values of  $p_c$  and  $T_c$  (which are easier and more accurately measured than  $v_c$ ) the constants  $a$  and  $b$  can be determined

$$a = \frac{27}{64} \frac{R^2 T_c}{p_c} \quad (7-17a)$$

$$b = \frac{1}{8} \frac{R T_c}{p_c} \quad (7-17b)$$

Some knowledge as to the validity of van der Waals' equation can be found by computing what is called the critical ratio  $r_c$

$$r_c = \frac{p_c v_c}{R T_c} \quad (7-18)$$

When the critical values for van der Waals' equation in terms of  $a$  and  $b$  are substituted in Eq (7-18),

$$r_c = \frac{p_c v_c}{R T_c} = 0.375$$

For the simple-gas law obviously

$$r_c = 1.0$$

Values for the critical ratio are listed in Table VII (Appendix). An average value for many gases is about 0.27. Hence, the perfect-gas

law will be far in error if applied to gases that are in a state at or near the critical point, while van der Waals' equation will at least approach the true conditions

**7-9. Other Equations of State** A great number of equations of state have been proposed. Some of these equations were derived on the basis of the kinetic theory of gases while others were adapted to fit observed data. The more famous of such equations will be discussed here.

*Dieterici* (1899)

$$p = \frac{RT}{v - b} e^{-a/RTv} \quad (7-19)$$

The constants  $a$  and  $b$  are evaluated in the same manner as shown in Art. 7-8

$$a = \frac{4R^2T_c^2}{p_c e^2}$$

$$b = \frac{RT_c}{p_c e^2}$$

In terms of these constants

$$p_c = \frac{a}{4e^2b^2} \quad v_c = 2b \quad T_c = \frac{a}{4Rb} \quad r_c = 0.27$$

Note that the value for the Dieterici critical ratio is equal to the most usual value for gases.

A revised<sup>1</sup> form of the Dieterici equation has the term  $RTv$  replaced by  $T^{1.27}v$ , and it reproduces quite well the experimental data for fluids in the neighborhood of their critical temperatures (Fig. 7-7).

*Onnes* (1901)

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \quad (7-20)$$

This equation is of historical interest and represents probably the first "open" or series form of the equation of state. Usually, the series is in powers of either specific volume or pressure and the coefficients  $A$ ,  $B$ , etc., are called the first, second, etc., *virial coefficients*. These coefficients are functions of temperature and not constants.

*Berthelot* (1903)

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \quad (7-21)$$

The constants  $a$  and  $b$  are evaluated

$$a = \frac{27}{64} \frac{R^2T_c^3}{p_c}$$

$$b = \frac{1}{8} \frac{RT_c}{p_c}$$

<sup>1</sup> Reference 1



In terms of these constants

$$p_c = \left( \frac{1}{216} \frac{aR^3}{b} \right)^{\frac{1}{3}} \quad v_c = 3b \quad T_c = \left( \frac{8abR}{27} \right)^{\frac{1}{3}} \quad r_c = 0.376$$

The Berthelot equation is a modified form of van der Waals' equation, and it is recommended<sup>1</sup> for use at temperatures considerably above the critical temperature of the gas in question (Fig. 7-8). Note that the Berthelot and the van der Waals' critical ratios have the same value.

*Beattie-Bridgeman* (1928)

$$p = RT \left( \frac{1 - e}{v^2} \right) (v + B) - \frac{A}{v^2} \quad (7-22)$$

$$\text{where } A = A_0 \left( 1 - \frac{a}{v} \right) \quad B = B_0 \left( 1 - \frac{b}{v} \right) \quad e = \frac{c}{vT^3}$$

This equation is the most accurate of the equations presented in this section. The constants were empirically selected to enable the equation to portray the known experimental data on many fluids (Table VIII, Appendix). The Beattie-Bridgeman equation can be rearranged into a form similar to the Onnes equation.

**7-10. Compressibility Factors.** The perfect-gas law can be extended to define more exactly the state of a fluid by use of a *compressibility factor*  $Z$  where

$$pv = ZRT \quad (7-23)$$

The factor  $Z$  is an empirical correction factor to align the observed data into the form of a simple equation. Such an equation can be used only as a point equation because  $Z$  is not a constant but an unknown function of both temperature and pressure.

In Fig. 7-7 the values of  $Z$  for carbon dioxide and ethylene are plotted against pressure for a temperature of 0°C. At this temperature carbon dioxide and, also, ethylene are liquids, except under relatively low pressures, and both fluids are close to their critical temperatures. Values of  $Z$ , shown in Fig. 7-7, were obtained from experimental data and also from three of the equations of state.

In Fig. 7-7 note that  $Z$  is 1.0 at zero pressure, for at zero pressure the volume is infinite and the fluids behave as perfect gases ( $pv = RT$ ). As the pressure is increased, the volume will rapidly decrease, because the fluids are near the two-phase regions of high density (note Figs. 6-1 and 6-3) and the effect of molecular attraction is considerable. If the temperature were the critical temperature instead of 0°C, the curve for each equation of state would descend to the critical ratio dictated by the form of the equation. As the pressure is increased to

<sup>1</sup> Reference 1

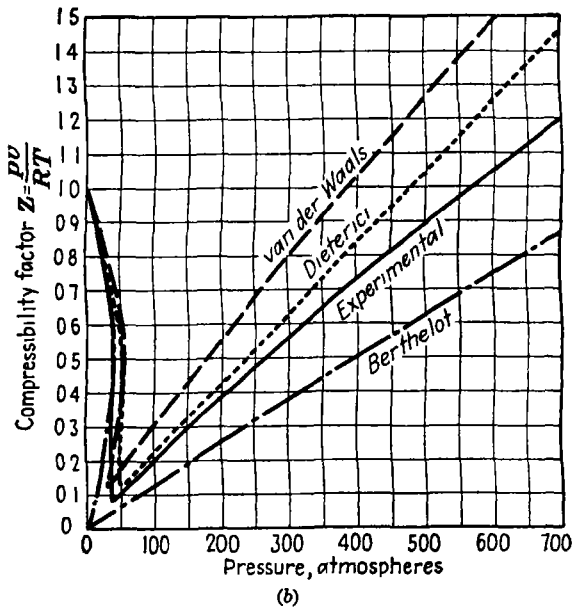
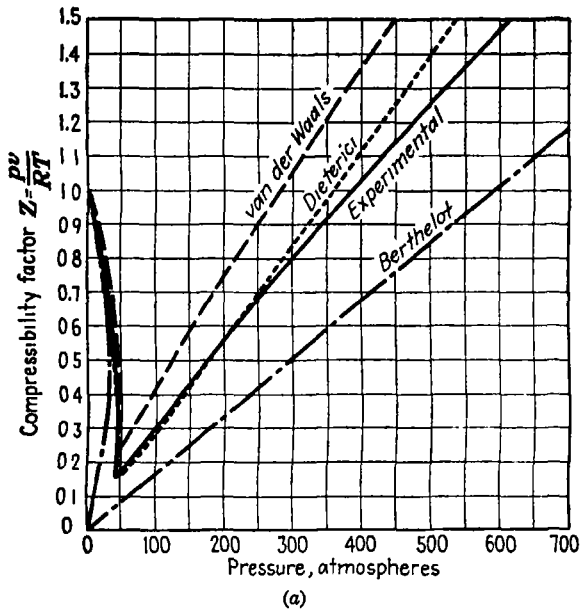


FIG. 7-7 Behavior of fluids near the critical temperature from experimental data and as predicted by equations of state (from reference 1) (a) Ethylene at  $0^\circ\text{C}$  ( $t_c = 9.6^\circ\text{C}$ ,  $p_c = 50.7\text{ atm}$ ) (b) Carbon dioxide at  $0^\circ\text{C}$  ( $t_c = 31^\circ\text{C}$ ,  $p_c = 73\text{ atm}$ )

still higher values, the volume cannot change as rapidly as before because the finite volume of the molecules is an increasingly larger fraction of the total volume. This is shown by the experimental curve for carbon dioxide. Since this fluid, for the temperature and pressure under consideration, is in the liquid state, it is relatively incompressible, and, in the high-pressure region,  $Z$  is closely proportional to pressure.

When the entire range of pressure in Fig 7-7 is considered, it is noted that the Dieterici equation reproduces best the experimental data.

Figure 7-8 differs from Fig 7-7 in that the gases shown are at a temperature that is considerably higher than the critical temperatures; a region of high density is not attained until the pressure is high and the decrease in  $Z$ , evident in Fig 7-7 at low pressures, is largely avoided.

Inspection of Fig 7-8 shows that Berthelot's and van der Waals' equations appear to fit the experimental data best at low and medium pressures.

**Example 7:** Determine the volume occupied by 1 lb<sub>m</sub> of nitrogen at a temperature of 32 F if the pressure is 500 atm.

**Solution:** For this temperature and pressure, Fig 7-8 shows the compressibility factor to be 1.39, hence,

$$v = \frac{ZRT}{p} = \frac{1.39(0.73)(492)}{500(28)} = 0.0357 \text{ ft}^3/\text{lb}_m \quad \text{Ans}$$

Note that the simple-gas law is 39 per cent in error.

**7-11. The Law of Corresponding States.** While it is entirely possible that for each fluid experimental data can be collected to develop either compressibility data or an equation of state, in many industrial cases such data are lacking. Either to wait for the appearance of such information or else to spend the time and money necessary for the development of the data may not be feasible, and a close approximation to the properties of a fluid may be acceptable.

All gases display characteristics that depend upon the location of the state on the  $pvT$  surface. When the state is close to a two-phase region, the characteristics are far different than when the state is in the superheat region (compare Fig 7-7 and 7-8). Van der Waals premised that the characteristics of all fluids could be shown by an equation of state that was based upon *corresponding states*. A *corresponding state* means that the state of one fluid on its  $pvT$  surface is in relatively the same location as the state of some other fluid on a differ-

ent-valued  $pvT$  surface. For example, if both fluids are at their respective critical points, the two states are *corresponding states*

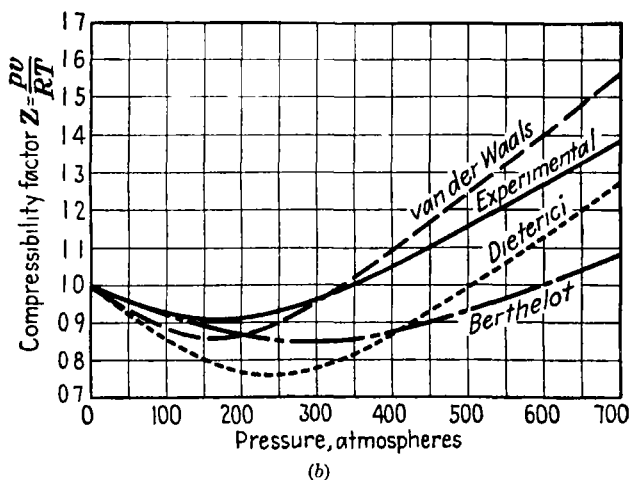
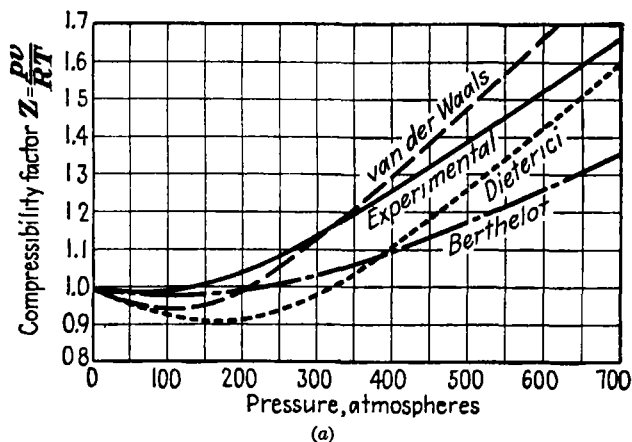


FIG 7-8 Behavior of fluids far above the critical temperature from experimental data and as predicted by equations of state (from reference 1) (a) Oxygen at 0°C ( $t_c = -118.8^\circ\text{C}$ ,  $p_c = 49.7\text{ atm}$ ) (b) Nitrogen at 0°C ( $t_c = -147.1^\circ\text{C}$ ,  $p_c = 33.5\text{ atm}$ ).

To reduce two different fluids to corresponding states, the properties can be expressed in terms of their critical points. The *reduced properties* are

$$p_r = \frac{p}{p_c} \quad T_r = \frac{T}{T_c} \quad v_r = \frac{v}{v_c} \quad (7-24)$$

If two or more fluids have the same value for their reduced properties,

the fluids are said to be in corresponding states. However, the reduced volume is rarely used because the critical volume is difficult to measure accurately.

In some instances the critical properties are empirically changed before the reduced properties are calculated. An empirically obtained critical property is called a *pseudocritical* property. For example, Newton<sup>1</sup> found that for hydrogen and helium better correlation could be obtained with other fluids if

$$\begin{aligned} T_{c'} &= T_c + 8 && \text{(Hydrogen and helium only,} \\ p_{c'} &= p_c + 8 && \text{for } T \text{ in degrees Kelvin and} \\ &&& p \text{ in atmospheres)} \end{aligned} \quad (7-25)$$

where the primed subscripts indicate a pseudocritical property

**7-12. Generalized Compressibility Factors.** If the compressibility factors for various gases are plotted in terms of reduced pressure and reduced temperature, it is found that the data for most gases will correlate quite closely. In Fig 7-9<sup>2</sup> a series of reduced temperature curves for hydrocarbons are shown on a plot of  $Z$  versus reduced pressure. The experimental data for 10 different gases are superimposed on this chart with an over-all average deviation for all fluids of the order of 1 per cent

**Example 8:** Determine by means of Fig 7-9 the pressure exerted by 1 lb<sub>m</sub> of CO<sub>2</sub> at 212 F if the specific volume is 0.193 ft<sup>3</sup> lb<sub>m</sub><sup>-1</sup>

**Solution:** Inspection of Fig 7-9 indicates that the solution must be made by a series of approximations because both  $Z$  and  $p$  are unknown. [Note, however, that there can be only one answer since two relationships are available for the two unknowns. These relationships are the generalized  $Z$  chart or  $Z = f(p_r, T_r)$  and the defining equation for  $Z$  or  $Z = pv/RT$ .] An approximation to the answer could be made by using the perfect-gas law, however, Example 6 for this same data gave  $p = 50.1$  atm by van der Waals' semiempirical equation

From Table VII (Appendix)

$$p_c = 73 \text{ atm}$$

$$t_c = 87.9 \text{ F}$$

Hence,

$$p_r = \frac{p}{p_c} = \frac{50}{73} = 0.685$$

$$T_r = \frac{T}{T_c} = \frac{459.7 + 212}{459.7 + 87.9} = 1.23$$

<sup>1</sup> NEWTON, R. H. Activity Coefficients for Gases, *Ind Eng Chem*, **27** (No. 3), 302-306 (March, 1935)

<sup>2</sup> GOUQ-JEN SU. Modified Law of Corresponding States for Real Gases, *Ind Eng Chem*, **38** (No. 8), 803-806 (August, 1946)

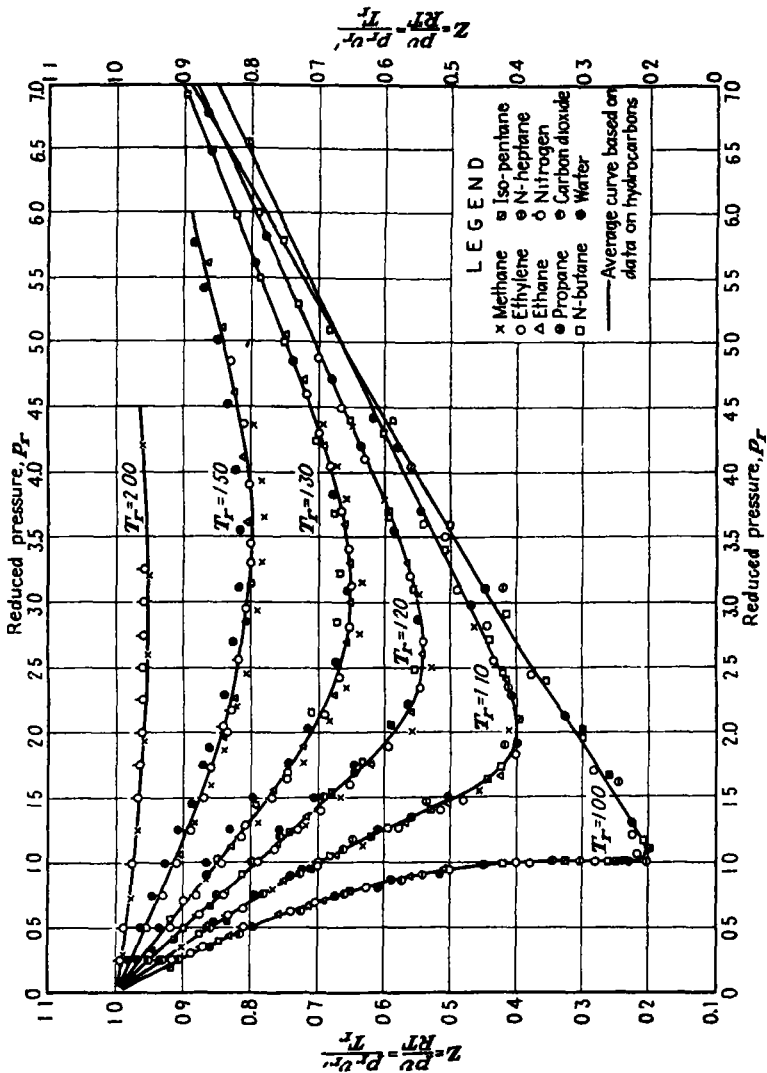


FIG 7-9 The generalized compressibility chart showing data for various gases (Gou-Jen Su Modified Law of Corresponding States for Real Gases, *Ind Eng Chem*, 38 (No 8), 803-806 August 1946)

From Fig 7-9 for these values,

$$Z = 0.88$$

From Eq (7-23),

$$p = \frac{ZRT}{v} = \frac{(0.88)(0.73)(671.7)}{(44)(0.193)} = 50.9 \text{ atm} \quad \text{Ans}$$

This answer is more accurate than that found by van der Waals' equation because

Fig 7-9 is known to represent  $\text{CO}_2$  quite accurately However, the van der Waals' answer is a very close approximation

In Fig 7-9 the generalized compressibility factor is shown to be a function of the reduced temperature and pressure It would seem that, if two gases are in corresponding states, both would have the same compressibility factor, yet this is not true, for by definition

$$Z = \frac{pv}{RT} \quad (7-23)$$

and the law of corresponding states requires

$$p = p_r p_c \quad T = T_r T_c \quad v = v_r v_c$$

When these values are substituted in Eq (7-23),

$$Z = \left( \frac{p_r v_r}{T_r} \right) \left( \frac{p_c v_c}{RT_c} \right)$$

If two gases are in corresponding states, the value of the first term in this equation,  $p_r v_r / T_r$ , will be the same for both fluids The value of the second term  $p_c v_c / RT_c$  is known from experimental data to vary widely for different fluids For example, consider steam and carbon dioxide These two fluids correlate each other on the  $Z$  chart within 2 per cent For the same corresponding states

$$\frac{p_c v_c}{RT_c} = 0.232 \quad \text{steam}$$

$$\frac{p_c v_c}{RT_c} = 0.28 \quad \text{CO}_2$$

$$\text{Difference} = 0.048, \text{ or } \frac{0.048}{0.28} = 17 \text{ per cent}$$

Thus, when steam and carbon dioxide are in corresponding states defined by Eq (7-24), the values of the compressibility factors for these fluids will vary by 17 per cent Because of this, reduced-volume lines cannot be shown on Fig 7-9 unless an error of approximately 17 per cent can be tolerated In other words, the generalized compressibility chart is more accurate than van der Waals' law of corresponding states

To remedy this difficulty, a pseudocritical volume called the ideal critical volume has been proposed<sup>1</sup>

<sup>1</sup> Su, p 200, see also reference 3

$$v_{c'} = \frac{RT_c}{p_c} \quad (7-26)$$

With this pseudocritical volume and the critical pressure and temperature a modified law of corresponding states is defined

$$p_r = \frac{p}{p_c} \quad (7-27a)$$

$$T_r = \frac{T}{T_c} \quad (7-27b)$$

$$v_{r'} = \frac{v}{v_{c'}} = \frac{p_c v}{RT_c} \quad (7-27c)$$

and

$$\begin{aligned} v_{r'} &= \frac{ZRT/p}{RT_c/p_c} = Z \frac{T_r}{p_r} \\ Z &= \frac{p_r v_{r'}}{T_r} \end{aligned} \quad (7-28)$$

Equation (7-28) proves that two gases in corresponding states defined by Eqs (7-27) have identical values for their compressibility factors.

With the aid of Eq (7-28) pseudoreduced volume lines can be added to the generalized compressibility chart. Figures VII and VIII (Appendix) are the result.

**Example 9** A mole of methane has a specific volume of  $2.2 \text{ ft}^3 \text{ mole}^{-1}$  and a temperature of  $515 \text{ R}$ . What pressure will be exerted?

**Solution** From Table VII (Appendix) for methane,

$$\begin{aligned} p_c &= 45.8 \text{ atm} \\ T_c &= 343.9 \text{ R} \\ T_r &= \frac{T}{T_c} = \frac{515}{343.9} = 1.5 \\ v_{r'} &= \frac{p_c v}{RT_c} = \frac{45.8(2.2)}{0.73(343.9)} = 0.40 \end{aligned}$$

From Fig. VII (Appendix) for these values,

$$Z = 0.803$$

and

$$\begin{aligned} p_r &= 3.0 \quad \text{or} \quad p = p_r p_c = 3.0(45.8) \\ &= 137 \text{ atm} \quad \text{Ans} \end{aligned}$$

By the perfect-gas equation

$$\begin{aligned} p &= \frac{RT}{v} = \frac{0.73(515)}{2.2} = 174 \text{ atm} \\ \text{Percentage error} &= 27 \text{ per cent} \end{aligned}$$

**Example 10:** Outline the procedure to be followed to find the isothermal work of a nonflow process by use of the compressibility factors.



**Solution :** For any fluid in a nonflow process

$$W_{\text{rev}} = \int p dv \quad (k)$$

The compressibility factor  $Z$  is defined

$$pv = ZRT$$

When the value of  $p$  is substituted in Eq (k),

$$W_{\text{rev}} = \int ZRT \frac{dv}{v}$$

The expansion is isothermal, hence,

$$W_{\text{rev}} = RT \int_{v_1}^{v_2} Z \frac{dv}{v} \quad (l)$$

This integration must be graphically performed because a function relating  $Z$  to  $v$  is not available. When Eq (l) is rewritten,

$$W_{\text{rev}} = RT \int Z d(\ln v) = RT \int Z dx$$

where  $x = \ln v$

Suppose the initial conditions of temperature and pressure are known. Then, for these initial conditions a value of  $Z$  and  $v_r$  can be obtained from Fig VII or VIII (Appendix). Several other values for these factors can be selected along an isotherm and at decreasing values for  $p_r$  (for an expansion process). After converting the reduced value of volume to true volume,  $\log v$  can be plotted against the corresponding value for  $Z$  in the manner illustrated in Fig A. The area under the curve in Fig A can be measured by a planimeter and then converted to the proper units. This area multiplied by  $RT$  is the work done (because the area is the  $\int Z dv/v$ ).

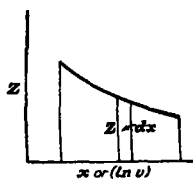


FIG A

**7-13. Generalized Equation of State.** Although a generalized equation of state could be developed from Eqs (7-24), the validity of the  $Z$  chart indicates that a more accurate equation<sup>1</sup> can be developed from the modified law of corresponding states [Eqs (7-27)]. To construct a generalized equation of state in the form of van der Waals' equation, substitute in the reduced Eqs (7-27) the values found for  $p_c$  and  $T_c$  in Art 7-8, namely,

$$p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR}$$

<sup>1</sup> See, p 200

This will give

$$p = p_r \frac{a}{27b^2} \quad T = T_r \frac{8a}{27bR} \quad v = v_r 8b$$

These values can be substituted into van der Waals' equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (7-13b)$$

and will result in

$$p_r = \frac{T_r}{v_r' - \frac{1}{8}} - \frac{\frac{27}{4}}{v_r'^2} \quad (7-29)$$

This is a universal equation with fixed constants that is applicable to all gases. All terms of the equation will be exactly the same as van der Waals' unreduced equation because the constants bear the same relationships to the critical pressure and temperature.

### Problems

The answers for these problems should be in the following units: pressure, psia and atm, temperature, R and F, volume, ft<sup>3</sup> mole<sup>-1</sup> and ft<sup>3</sup> lb<sub>m</sub><sup>-1</sup>. Normal atmospheric pressure is 14.7 psia.

#### PERFECT-GAS EQUATIONS (Use Table VI, Appendix)

1. (a) The specific volume of a gas is 5 ft<sup>3</sup> lb<sub>m</sub><sup>-1</sup>, determine the density ( $M = 30$ ). (b) Determine the density of a gas if the volume is 20 ft<sup>3</sup>, mass is 2 lb, and  $M$  is 20.

2. Repeat the derivation in Art. 7-2, using the engineering dimensional system and  $g_c$ .

3. Determine the density and specific volume of a gas if the volume is 400 ft<sup>3</sup>, the number of moles is 2, and  $M = 40$ .

4. If the pressure is atmospheric, determine the temperature of the gases in Probs. 1, 2, and 3.

5. A volume of 3 ft<sup>3</sup> of gas under atmospheric pressure has the pressure doubled while the temperature remains constant. What is the final volume for the gas?

6. Repeat Prob. 5, assuming that the volume doubles while the temperature remains constant, and find the final pressure.

7. A volume of 5 cu ft of gas at 200 F and 20 psia is expanded at constant pressure to a final volume of 10 ft<sup>3</sup>. Determine the final temperature.

8. If the gas in Prob. 7 is air, how many pounds (and moles) are present? Repeat, assuming that methane is the fluid.

9. A pound of air at a pressure of 100 psia and temperature of 60 F is to be stored in a tank. How large must the tank be? Repeat, assuming that methane is the fluid.

10. Repeat Prob. 9, assuming that the mass unit is the mole.

11. A tank containing air at 60 psia and 60 F is exposed to the sun and absorbs radiant energy until the temperature is 130 F. What will be the final pressure?

12. A 10-ft<sup>3</sup> tank contains air at 20 psia and 60 F. Air is pumped into the tank until the pressure is 100 psia and temperature 150 F. How much air was pumped into the tank?

**13.** A 10-ft<sup>3</sup> tank containing 0.25 lb<sub>m</sub> of air at 60 F is connected to a similar tank that is at the same temperature but contains 0.50 lb<sub>m</sub> of air. Determine the resultant pressure

**14.** A reservoir contains 100 ft<sup>3</sup> of air at 1,000 psia and 100 F. Another tank is filled from the reservoir to a pressure of 50 psia and temperature of 60 F while the pressure in the reservoir decreases to 900 psia and the temperature to 80 F. What is the volume of the tank?

**15.** A tank contains air at a pressure of 100 psia and 60 F. A pound of air is removed from the tank, and this causes the final conditions in the tank to be 50 psia and 50 F. What is the volume of the tank?

**16.** In a steady-flow process air enters a system at 60 F and leaves at 200 F while 10 Btu lb<sub>m</sub><sup>-1</sup> of work is done by the system. How much heat was transferred to the system?

**17.** In a nonflow process a mole of air is adiabatically compressed from  $p = 15$  psia and  $t = 60$  F to a temperature of 200 F. How much work was transferred?

**18.** In a nonflow process 1 lb<sub>m</sub> of methane at a pressure of 15 psia and a temperature of 80 F is compressed to 300 F while 10 Btu mole<sup>-1</sup> of heat is removed from the system. How much work was transferred?

**19.** In a nonflow adiabatic process, work is transferred to a system, of amount 10 Btu lb<sub>m</sub><sup>-1</sup>, while air is compressed from  $t = 80$  F and  $p = 15$  psia to  $p = 100$  psia. What will be the final temperature?

In the following problems, use the heat-capacity equations of Table IIB (Appendix).

**20.** Repeat Prob 11, Chap IV

**21.** Repeat Prob 12, Chap IV

**22.** Repeat Prob 13, Chap IV

**23.** Repeat Prob 14, Chap IV

**24.** Repeat Prob 15, Chap IV

**25.** Repeat Prob 16, Chap IV

**26.** Repeat Prob 17, Chap IV

**27.** Repeat Prob 18, Chap IV

#### PERFECT AND IMPERFECT GASES

**28.** Compute, using van der Waals' equation, the pressure exerted by 2 lb<sub>m</sub> air at 100 F if the volume is 30 ft<sup>3</sup>. Compare the answer with that found from the perfect-gas equation

**29.** Repeat Prob 28, assuming that methane is the fluid

**30.** A pound of carbon dioxide has a volume of 0.15 ft<sup>3</sup> and a pressure of 100 atm. Compute the temperature, using van der Waals' and the perfect-gas equations

**31.** Repeat Prob 30, assuming that methane is the fluid

**32.** Compute, using van der Waals' equation, the volume occupied by 1 lb<sub>m</sub> of CO<sub>2</sub> at  $p = 4,000$  psia and  $t = 200$  F, and compare the answer to that found by the perfect-gas equation

**33.** Determine the volume occupied by 1 lb<sub>m</sub> of CO<sub>2</sub> at a temperature of 100 F and pressure of 1,000 atm (compressibility chart, Fig VII or VIII, Appendix)

**34.** Repeat Prob 28, using the compressibility factor

**35.** Repeat Prob 29, using the compressibility factor

36. Repeat Prob 30, using the compressibility factor
37. Repeat Prob 31, using the compressibility factor
38. Repeat Prob 32, using the compressibility factor
39. Evaluate the constants  $a$  and  $b$  in the Dieterici equation to check the values given in Art 7-9
40. Repeat Prob 39, using the modified equation
41. Expand the Beattie-Bridgeman equation by inserting all terms and show that it is a form of the Onnes equation
42. Repeat Prob 39, using the Berthelot equation
43. Determine by the method of Example 10 the nonflow work necessary to compress carbon dioxide isothermally from 1,000 to 4,000 psia and at a temperature of 140 F

## Symbols

$a$	constant
$A$	constant
$b$	constant
$B$	constant
$e$	base of the natural logarithm, also, a constant
$F$	force
$F$	degrees Fahrenheit
g-mole	gram mole
$h$	enthalpy (specific)
$k$	ratio of $c_p$ to $c_v$
$K$	Kelvin temperature scale
KE	kinetic energy
$m$	mass, also, mass of one molecule
mole	pound mole
$M$	molecular weight
$n'$	number of molecules
$n$	number, also, number of molecules per unit volume
$p$	pressure
$Q$	heat
$r$	ratio
$R$	degrees Rankine
$R$	universal or specific gas constant (mechanical or thermal units)
$R_0$	universal gas constant (mechanical or thermal units)
$t$	thermodynamic temperature
$T$	absolute thermodynamic temperature
$u$	internal energy (specific)
$V$	volume, also, velocity
$v$	specific volume
$W$	work
$z$	distance
$Z$	compressibility factor

## Subscripts

$A$	added, also, gas $A$
avg	average
$B$	gas $B$

$c$	critical state
$c'$	pseudocritical state
$p$	constant pressure
$R$	rejected
$r$	reduced property
$r'$	pseudoreduced property
$v$	constant volume
$x$	coordinate direction
$y$	coordinate direction
$z$	coordinate direction

#### Greek Letters

$\rho$	(rho)	density
$\Sigma$	(sigma)	summation

#### Suggested References

- 1 BUREAU OF STANDARDS "Relations between the Temperatures, Pressures, and Densities of Gases," Circular 279 (1926)
- 2 DODGE, B. F. "Chemical Engineering Thermodynamics," Chap. 5, McGraw-Hill Book Company, Inc., New York, 1944
- 3 WEBER, H. C. "Thermodynamics for Chemical Engineers," Chap. 8, John Wiley & Sons, Inc., New York, 1939
- 4 ELLENWOOD, F. O., N. KULIK, and N. R. GAY "The Specific Heats of Certain Gases over Wide Ranges in Temperature and Pressure," Cornell University Bulletin, No. 30, October, 1942

**CLASS ASSIGNMENTS**



## CHAPTER VIII

### APPROXIMATE CALCULATIONS FOR REAL GASES

The concept of a perfect gas represents a limiting state that can be approached but not attained by any real gas. However, in mechanical engineering many of the processes are conducted at such pressures and temperatures that the perfect-gas laws can be used as a simple and reasonably close approximation to the behavior of the real fluid. This is especially true when the medium is air, since at normal atmospheric temperatures the error in this approximation to the true equation of state is of the order of 1 per cent at 300 psi and 0.1 per cent at atmospheric pressure. At higher temperatures the error becomes progressively smaller.

**8-1. Relationships for Real or Perfect Gases.** Because of the number of relationships that will be developed in this chapter, it may be desirable to summarize here those relationships that were previously developed for either real or ideal fluids. As a result of the first two laws and for either flow or nonflow processes,

$$Q - W = de \quad (3-1)$$

$$Tds = du + pdv \quad (5-14a)$$

$$Tds = dh - vdp \quad (5-14b)$$

and, with the restriction that the process must be reversible,

$$Q_{\text{rev}} = \int Tds \quad (5-5)$$

$$W_{\text{rev nonflow}} = \int pdv \quad (4-1)$$

$$W_{\text{rev steady flow}} = \int pdv - \Delta FE - \Delta KE = - \int vdp - \Delta KE \quad (4-3)$$

$$ds = \left. \frac{dQ}{T} \right]_{\text{rev}} \quad (5-4)$$

while, by definition of the heat capacity (for reversible or irreversible processes)

$$dh \Big|_{p=c} = c_p dT \quad (4-6)$$

$$du \Big|_{v=c} = c_v dT \quad (4-7)$$



and for reversible processes

$$dQ_{rev} = c_s dT \quad (4-5)$$

All the above equations are for unit mass of fluid

**8-2. Relationships for the Perfect Gas.** Upon the structure of general equations listed in Art 8-1, certain restrictions can be placed to obtain the simple relationships for the perfect gas. Such a gas will obey the following equations

$$pv = RT \quad (7-3a)$$

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad (7-2)$$

$$du = c_v dT \quad (7-7)$$

$$dh = c_p dT \quad (7-8)$$

$$c_p - c_v = R \quad (7-9)$$

$$k = \frac{c_p}{c_v} \quad (7-10)$$

$$c_p = \frac{kR}{k-1} \quad (7-11)$$

$$c_v = \frac{R}{k-1} \quad (7-12)$$

System equations can be developed for perfect gases by substituting Eqs (7-7) and (7-8) in Eqs (5-14a) and (5-14b)

$$Tds = c_v dT + pdv \quad (8-1)$$

$$Tds = c_p dT - vdp \quad (8-2)$$

From these equations and Eq (7-3a)

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \quad (8-3)$$

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p} \quad (8-4)$$

The equation of state can be differentiated and divided by the temperature  $T$  and gas constant  $R$

$$\frac{pdv}{RT} + \frac{vdp}{RT} = \frac{RdT}{RT}$$

or

$$\frac{dv}{v} + \frac{dp}{p} = \frac{dT}{T} \quad (8-5)$$

With this relationship and Eq (7-9) substituted in either Eq (8-3)

or (8-4),

$$ds = c_p \frac{dv}{v} + c_v \frac{dp}{p} \quad (8-6)$$

For simplicity of presentation, the heat capacities will be considered, most often, to be constants

**8-3. Constant Volume and Constant Pressure Processes.** The equations listed and developed in Art 8-1 and 8-2 furnish adequate information for finding more restricted expressions for the special processes at constant volume and constant pressure. The procedure to be followed (but not answers to be memorized) will be illustrated here. From Eq (7-2)

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

*Constant Volume*

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \text{and} \quad \frac{p_1}{p_2} = \frac{T_1}{T_2}$$

*Constant Pressure*

$$\frac{v_1}{T_1} = \frac{v_2}{T_2} \quad \text{and} \quad \frac{v_1}{v_2} = \frac{T_1}{T_2}$$

The work of the reversible process is found by Eq (4-1) or (4-3).

*Constant Volume*

$$W_{\text{rev nonflow}} = \int p dv = 0$$

because  $dv = 0$

$$\begin{aligned} W_{\text{rev flow}} &= - \int v dp - \Delta KE \\ &= - v(p_2 - p_1) - \Delta KE \\ &\quad \text{because } v = C \end{aligned}$$

*Constant Pressure*

$$W_{\text{rev nonflow}} = \int p dv = p(v_2 - v_1)$$

because  $p = C$

$$\begin{aligned} W_{\text{rev flow}} &= - \int v dp - \Delta KE \\ &= - \Delta KE \\ &\quad \text{because } dp = 0 \end{aligned}$$

The heat transfer for the reversible process is found by Eq (4-5) or from Eq (8-1)

*Constant Volume*

$$Q_{\text{rev}} = \int T ds = \int c_v dT$$

*Constant Pressure*

$$Q_{\text{rev}} = \int T ds = \int c_p dT$$

and, if the heat capacity is considered to be constant,

$$Q_{\text{rev}} = c_v(T_2 - T_1)$$

$$Q_{\text{rev}} = c_p(T_2 - T_1)$$

The change in entropy for the reversible or irreversible process is found from Eq (8-3) or (8-4) or from Eqs (5-4) and (4-5)

*Constant Volume*

$$ds = c_v \frac{dT}{T}$$

*Constant Pressure*

$$ds = c_p \frac{dT}{T}$$

and, if the heat capacity is considered to be constant,

$$\Delta s = c_v \ln \frac{T_2}{T_1} \qquad \Delta s = c_p \ln \frac{T_2}{T_1}$$

**Example 1:** A mole of gas at a pressure of 500 psia undergoes a constant-pressure nonflow process with the temperature changing from 1000 to 1100 R. What is the maximum amount of work that can be obtained from this expansion process?

**Solution** The maximum work is the reversible work

$$W_{\text{rev}} = \int p dv = p(v_2 - v_1) \text{ ft lb}_f/\text{lb}_m \qquad (a)$$

At any state

$$pv = RT$$

and upon substitution in (a)

$$W_{\text{rev}}]_{p=C} = R(T_2 - T_1)$$

The units for work will depend on the units selected for  $R$  (Table IV, Appendix)

$$\begin{aligned} W_{\text{rev}} &= (1.986 \text{ Btu/mole R}) (1100 - 1000) \text{ R} \\ &= 198.6 \text{ Btu/mole} = 154,500 \text{ ft lb}_f/\text{mole} \quad \text{Ans} \end{aligned}$$

**Example 2:** One pound of nitrogen at a temperature of 40 F is confined in a constant-volume container, heat is added, and the pressure increases from 20 to 40 psia. How much heat is transferred, and what is the value for the change in entropy?

**Solution** If the heat capacity is assumed to be constant, then, for a constant-volume change,

$$Q_{\text{rev}}]_{v=C} = c_v(T_2 - T_1) \qquad (a)$$

$$\Delta s]_{v=C} = c_v \ln \frac{T_2}{T_1} = c_v \ln \frac{p_2}{p_1} \qquad (b)$$

while from the equation of state

$$\begin{aligned} \frac{p_1}{p_2} &= \frac{T_1}{T_2} \\ \frac{20}{40} &= \frac{460 + 40}{T_2} \\ T_2 &= 1000 \text{ R} \end{aligned}$$

From Table VI (Appendix) and Eq. (7-9),

$$M_{N_2} = 28 \qquad c_p = 0.246 \text{ Btu/lb}_m \text{ R} \qquad c_p - c_v = R$$

Hence,

$$\begin{aligned} c_v &= c_p - R \\ &= 0.246 - \frac{1.986}{28} = 0.175 \text{ Btu/lb}_m \text{ R} \end{aligned}$$

When these values are substituted in Eqs. (a) and (b),

$$Q_{\text{rev}}]_{v=C} = c_v(T_2 - T_1) = 0.175(500) = 87.5 \text{ Btu/lb}_m \quad \text{Ans}$$

$$\Delta s = c_v \ln \frac{T_2}{T_1} = 0.175 \ln 2 = 0.121 \text{ Btu/lb}_m \text{ R} \quad \text{Ans}$$

It will be better to remember only the basic formulas and to make substitutions in the general formulas for each problem. In this problem a new equation could be derived

$$\begin{aligned} Q_{rev|v=C} &= c_v \left( \frac{p_2 v_2 - p_1 v_1}{R} \right) \\ &= \frac{c_v}{R} (p_2 v_2 - p_1 v_1) \\ &= \frac{c_v v_1}{R} (p_2 - p_1) = c_v T_1 \left( \frac{p_2 - p_1}{p_1} \right) \end{aligned}$$

which contains only known properties. However, the student should not attempt to memorize and use such equations. It will be better training to develop such relationships as a part of each problem.

**Example 3:** Repeat Example 2, but take into account the variation of heat capacity with temperature. (Note that this will be the proper solution for a perfect gas since the constancy of specific heat was adopted only for simplicity of presentation.)

**Solution:** From Table IIB (Appendix) and Eq. (7-9) the heat capacity of nitrogen at constant volume is

$$c_v = c_p - R = 7484 - \frac{347(10^3)}{T} + \frac{116(10^6)}{T^2} \text{ Btu/mole } R$$

The heat transferred is

$$\begin{aligned} Q_{rev|v=C} &= \int_{500}^{1000} c_v dT \\ &= \left[ 7484(T_2 - T_1) - 347(10^3) \ln \frac{T_2}{T_1} - 116(10^6) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \\ &= 2497 \text{ Btu/mole} \\ &= 89.2 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

The entropy change is

$$\begin{aligned} \Delta s|_{v=C} &= \int \frac{c_v dT}{T} \\ &= \int_{500}^{1000} \left[ \frac{7484}{T} - \frac{347(10^3)}{T^2} + \frac{116(10^6)}{T^3} \right] dT \\ &= 7484 \ln \frac{T_2}{T_1} + 347(10^3) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) - 0.58(10^6) \left( \frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \\ &= 5185 - 347 + 174 \\ &= 3455 \text{ Btu/mole } R \\ &= 0.123 \text{ Btu/lb}_m R \quad \text{Ans} \end{aligned}$$

**Example 4:** Assume that the fluid in Example 1 is carbon dioxide and van der Waals' equation will adequately portray the state of the gas. Compare the answer found from this equation of state with the answer found from the perfect-gas equation.

**Solution:** Van der Waals' equation is not explicit in  $v$ , hence,  $v_1$  and  $v_2$  must be determined by trial. With constants from Example 6, Chap. VII,

$$a = 924.2 \text{ atm ft}^3/\text{mole}^2 \quad b = 0.685 \text{ ft}^3/\text{mole} \quad R = 0.73 \text{ atm ft}^3/\text{R mole}$$

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$= \frac{0.73T}{(v-0.685)} - \frac{924.2}{v^2}$$

For the given conditions of  $T_1 = 1000 \text{ R}$  and  $p = 500 \text{ psia}$  or  $34 \text{ atm}$ ,

$$34 = \frac{730}{(v-0.685)} - \frac{924.2}{v^2} \quad (a)$$

The volume of a perfect gas for the initial conditions can be found from  $pv = RT$  and is  $21.45 \text{ ft}^3/\text{mole}^{-1}$ . The volume of the carbon dioxide should be of this order of magnitude. When Eq. (a) is solved by trial, the initial volume of  $\text{CO}_2$  is

$$v_1 = 20.9 \text{ ft}^3/\text{mole}$$

In a similar manner, at  $1100 \text{ R}$  the volume of  $\text{CO}_2$  is

$$v_2 = 23.2 \text{ ft}^3/\text{mole}$$

and therefore

$$W_{\text{rev}}]_{p=C} = p(v_2 - v_1)$$

$$= 500(144)(23.2 - 20.9)$$

$$= 165,500 \text{ ft lb}_f/\text{mole} = 213 \text{ Btu/mole} \quad \text{Ans}$$

This answer is more nearly correct than the perfect-gas solution, and the difference is

$$\text{Error} = \frac{213 - 198.6}{213} = 6.75 \text{ per cent} \quad \text{Ans}$$

**8-4. The Isothermal Process.** The isothermal or constant-temperature process for the perfect gas is a process at constant internal energy and, also, at constant enthalpy as is evident from inspection of Eqs. (7-7) and (7-8). Thus, in the absence of kinetic and potential effects the First Law when applied either to the isothermal flow or nonflow process shows

$$Q - W = 0$$

and

$$Q = W]_{\text{flow or nonflow}}^{\Delta KE \Delta PE = 0} \quad (8-7a)$$

The reversible transfer of heat cannot be evaluated from the heat-capacity equation [Eq. (4-5)] because the change of temperature is zero and therefore the heat capacity must be infinite. However, the work can be found by noting from Eq. (7-2) that

$$p_1 v_1 = p_2 v_2 = \text{constant for the process}$$

$$p = \frac{C}{v}$$

and

$$W_{\text{rev}} = \int p dv = C \int \frac{dv}{v} = RT \ln \frac{v_2}{v_1} = pv \ln \frac{p_1}{p_2} \quad (8-7b)$$

Equation (8-7a) shows the transfers of heat and work to be equal

The change in entropy for the isothermal process can be found from either Eq (8-3), (8-4), or (5-4)

$$\Delta s \Big|_{T=C} = R \ln \frac{v_2}{v_1} = R \ln \frac{p_1}{p_2} \quad (8-8)$$

**Example 5:** A mole of gas at a pressure of 500 psia undergoes an isothermal and reversible nonflow process at 1000 R until the volume is doubled. How much work and heat are transferred?

**Solution:** Equations (8-7a) and (8-7b) show that

$$\begin{aligned} Q_{\text{rev}} = W_{\text{rev}}|_{T=C} &= RT \ln \frac{v_2}{v_1} \\ &= 1.986(1000) \ln 2 \\ &= 1377 \text{ Btu/mole} \quad \text{Ans} \end{aligned}$$

and this value equals not only the work *done* by the system but also the heat *added* to the system

**Example 6:** Investigate the relationships between heat and work for a steady-flow and reversible isothermal process with kinetic-energy effects

**Solution:** The equation for the work of a steady-flow process with kinetic effects is Eq (4-3b)

$$W_{\text{rev}} = \int p dv - \Delta FE - \Delta KE = -\int v dp - \Delta KE$$

and for isothermal flow

$$\begin{aligned} W_{\text{rev}}|_{T=C} &= RT \ln \frac{v_2}{v_1} - (p_2 v_2 - p_1 v_1) - \Delta KE \\ W_{\text{rev}}|_{T=C} &= RT \ln \frac{v_2}{v_1} - \Delta KE \quad \text{Ans} \end{aligned}$$

The heat transferred is found by the First Law equation.

$$Q - W = \Delta e_{\text{flow}} = \Delta h + \Delta KE$$

and

$$\begin{aligned} Q_{\text{rev}}|_{T=C} &= \left( RT \ln \frac{v_2}{v_1} - \Delta KE \right) + \Delta h + \Delta KE \\ Q_{\text{rev}}|_{T=C} &= RT \ln \frac{v_2}{v_1} \quad \text{Ans} \end{aligned}$$

Thus, in this isothermal-flow process the transfers of heat and work are not equal. The same answer, of course, is found from the system equations (8-1) and (8-2).

$$\begin{aligned} Q_{\text{rev}} &= \int T ds = \int p dv = RT \ln \frac{v_2}{v_1} \\ Q_{\text{rev}} &= \int T ds = - \int v dp = RT \ln \frac{p_1}{p_2} \end{aligned}$$

Hence, for the isothermal process

$$\int p dv = - \int v dp$$

because  $p_1 v_1 = p_2 v_2$  or  $\Delta FE = 0$

**Example 7:** For the same conditions as in Example 5, find the work that can be done by 1 mole of carbon dioxide in a nonflow process

**Solution:** Assuming that van der Waals' equation will correctly show the relationships between pressure and volume in an isothermal process,

$$W_{rev} = \int p dv$$

and

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

Hence,

$$\begin{aligned} W_{rev} &= RT \int \frac{dv}{v-b} - a \int \frac{dv}{v^2} \\ &= RT \ln \frac{v_2-b}{v_1-b} + a \left( \frac{1}{v_2} - \frac{1}{v_1} \right) \end{aligned}$$

From Example 4 for these same conditions,

$$\begin{aligned} v_1 &= 20.9 \text{ ft}^3/\text{mole} & R &= 0.73 \text{ atm ft}^3/\text{R mole} \\ a &= 924.2 \text{ atm ft}^6/\text{mole}^2 & b &= 0.685 \text{ ft}^3/\text{mole} \end{aligned}$$

Hence,

$$\begin{aligned} \ln \frac{v_2-b}{v_1-b} &= \frac{41.8 - 0.685}{20.9 - 0.685} = 1.96 \\ W_{rev} &= 0.73(1000) \ln 1.96 + 924.2 \left( \frac{1}{41.8} - \frac{1}{20.9} \right) \\ &= 491 - 22.2 \\ &= 468.8 \text{ atm ft}^3/\text{mole} \\ &= 1271 \text{ Btu/mole} \quad \text{Ans} \end{aligned}$$

Since carbon dioxide deviates considerably from the perfect-gas laws, the change in internal energy for the isothermal process is not zero, and therefore the heat transferred is only approximately equal to the work done

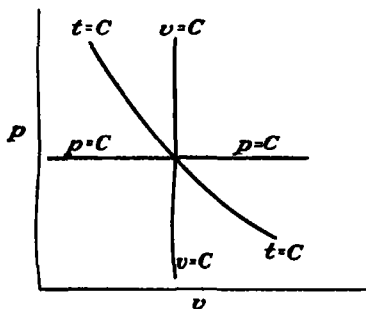


FIG. 8-1 Constant specific-volume, constant pressure, and constant temperature processes on the  $p$ - $v$  diagram

for all states encountered during the process. Such a *path equation* has already been found for the isothermal process

$$pv = C$$

### 8-5. The Polytropic Process.

The processes of the perfect gas at constant volume, constant pressure, and constant temperature are illustrated on the  $p$ - $v$  diagram of Fig 8-1. Since each process traces a path on the  $p$ - $v$  diagram, it should be possible to find an equation that interrelates the properties of pressure and volume

Equations of similar form can be constructed for the constant-volume and constant-pressure processes.

Constant volume  $p_1 v_1^n = p_2 v_2^n = C$  or  $p_1^{\frac{1}{n}} v_1 = p_2^{\frac{1}{n}} v_2$  or  $v_1 = v_2$

Constant pressure  $p_1 v_1^0 = p_2 v_2^0 = C$  or  $p_1 = p_2$

A general path equation can be proposed of the form

$$pv^n = C \text{ (constant)} \quad (8-9)$$

where

$n = \infty$  for constant volume

$n = 1$  for constant temperature

$n = 0$  for constant pressure

$n = \text{constant}$  for other processes

Since this equation involves only properties of the system (and does not involve the external effects of the system, heat and work), it can be used for reversible and, also, for most irreversible processes [unless it is impossible to define values for pressure and specific volume for the irreversible process (Art 4-4)]

Equation (8-9) does not attempt to trace every possible process on the  $pv$  diagram between two particular states for this would require the exponent  $n$  to be a variable that could assume many values throughout the process. However, by restricting  $n$  to a constant value, it is always possible to devise a path between any two states on the  $pv$  diagram (or, if desired, a series of paths). A process that follows the equation  $pv^n = C$  is called a *polytropic process* unless some property remains constant during the process, and then it is assigned a name to show the constancy of the property—constant volume, isothermal, etc

The  $pvT$  relationships between two states on a polytropic path can be determined from the *path* equation  $pv^n = C$  and the *equation of state*  $pv = RT$  (which is a *point* equation). For any two states

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad \text{or} \quad \frac{T_2}{T_1} = \frac{p_2 v_2}{p_1 v_1} \quad (a)$$

and either  $p$  or  $v$  can be eliminated by substituting

$$\frac{p_1}{p_2} = \left( \frac{v_2}{v_1} \right)^n \quad \text{or} \quad \frac{v_1}{v_2} = \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}} \quad (b)$$

to yield

$$\frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{n-1} \quad (8-10)$$

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \quad (8-11)$$



The work for a nonflow polytropic process is determined in the usual manner.

$$W_{\text{rev}} = \int p dv$$

Substitution, from the path equation  $pv^n = C$ , of

$$p = \frac{C}{v^n}$$

will give

$$W_{\text{rev}} = C \int \frac{dv}{v^n} = C \left( \frac{v^{-n+1}}{1-n} \right)_{v_1}^{v_2} = C \left( \frac{v_2^{1-n} - v_1^{1-n}}{1-n} \right)$$

But the constant  $C = p_1 v_1^n = p_2 v_2^n$  and upon substitution

$$\begin{aligned} W_{\text{rev nonflow}} &= \frac{p_2 v_2 - p_1 v_1}{1-n} = \frac{R(T_2 - T_1)}{1-n} = \frac{RT_1[(T_2/T_1) - 1]}{1-n} \\ &= \frac{RT_1}{1-n} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] \quad (8-12) \end{aligned}$$

The work for a steady-flow process is

$$W_{\text{rev steady flow}} = \int p dv - \Delta FE - \Delta KE$$

and this will be found to be

$$\left. \begin{aligned} W_{\text{rev steady flow}} &= \frac{n}{1-n} (p_2 v_2 - p_1 v_1) - \Delta KE \\ &= \frac{nR}{1-n} (T_2 - T_1) - \Delta KE \\ &= \frac{nRT_1}{1-n} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] - \Delta KE \end{aligned} \right\} \quad (8-13)$$

[Note that Eqs (8-13) differ from Eqs (8-12) by the factor  $n$  and the term for kinetic energy, while the units for  $R$  determine the units of work]

These equations show that the work of compression or expansion is independent of the final conditions and depends on the initial temperature and on the pressure ratio (while no assumptions need be made as to the mechanical details of the compressor). The same amount of work is realized from a pressure ratio of 100 to 10 psia, 1000 to 100 psia, or 1 to 0.1 psia.

An expression for the heat transferred during a reversible polytropic flow or nonflow process can be found from the system equation

(8-1). For simplicity the heat capacities will be considered to be constants

$$Q_{\text{rev}} = \int T ds = c_v(T_2 - T_1) + \int p dv$$

The  $\int p dv$  has been evaluated as Eq (8-12), hence,

$$\begin{aligned} Q_{\text{rev}} &= c_v(T_2 - T_1) + \frac{R(T_2 - T_1)}{1 - n} \\ &= \frac{[c_v(1 - n) + R](T_2 - T_1)}{1 - n} \end{aligned}$$

When Eqs. (7-9) and (7-10) are substituted,

$$\begin{aligned} Q_{\text{rev}} &= \frac{c_p - nc_v}{1 - n} (T_2 - T_1) \\ Q_{\text{rev}} &= c_v \left( \frac{k - n}{1 - n} \right) (T_2 - T_1) \end{aligned} \quad (8-14)$$

Comparison of this equation with Eq (4-5) shows that a polytropic heat capacity can be defined as

$$c_n = c_v \left( \frac{k - n}{1 - n} \right) \quad (8-15)$$

Note that the term  $c_n$  is a property for either the reversible or irreversible process, but it can be used to determine the heat transfer only for the reversible process

The change in entropy for any polytropic process can be simply found from the above equation

$$\begin{aligned} \Delta s &= \int \frac{c_n dT}{T} \\ &= c_n \ln \frac{T_2}{T_1} = c_v \left( \frac{k - n}{1 - n} \right) \ln \frac{T_2}{T_1} \end{aligned} \quad (8-16)$$

**Example 8:** Air is compressed in a nonflow process along a reversible polytropic path for which  $n$  is 1.3. Find the heat and work transferred if the initial pressure is atmospheric at a temperature of 60 F and the final pressure is 125 psia.

**Solution:** For this polytropic process Eq (8-12) is applicable

$$\begin{aligned} W_{\text{rev}} &= \frac{RT_1}{1 - n} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] \quad (M_{\text{air}} = 29) \\ &= - \frac{1545(520)}{29(0.3)} \left[ \left( \frac{125}{14.7} \right)^{0.231} - 1 \right] \\ &= -59,100 \text{ ft lb}_f/\text{lb}_m \quad \text{Ans} \end{aligned}$$

The heat transferred is found from Eq (8-14)

$$\begin{aligned} Q_{\text{rev}} &= c_v \left( \frac{k-n}{1-n} \right) (T_2 - T_1) \\ &= 0.171 \left( \frac{1.4-1.3}{1-1.3} \right) (T_2 - 520) \end{aligned}$$

where  $T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} = 520(1.64) = 853 \text{ R}$

$$Q_{\text{rev}} = -19.0 \text{ Btu/lb}_m \quad \text{Ans}$$

**8-6. The Isentropic Process.** The path equation for the reversible adiabatic process can be found from the polytropic equation (8-14) by noting that for the adiabatic process no heat is transferred

$$Q_{\text{rev}} = 0 = c_v \left( \frac{k-n}{1-n} \right) (T_2 - T_1)$$

Since  $c_v$  and  $T_2 - T_1$  are not zero,  $k - n$  must be zero or

$$n = k$$

The equation for the isentropic path is thus

$$pv^k = C \quad (8-17)$$

This equation can be readily verified from Eq (8-6) for the condition that the heat capacities are constant

$$ds = c_p \frac{dv}{v} + c_v \frac{dp}{p} = 0 \quad (8-6)$$

Dividing by  $c_v$  and transposing,

$$k \frac{dv}{v} = - \frac{dp}{p}$$

which integrates to

$$\left( \frac{v_2}{v_1} \right)^k = \frac{p_1}{p_2}$$

and

$$p_1 v_1^k = p_2 v_2^k = C \quad (8-17)$$

This equation does not restrict the process to be reversible. For example, an irreversible expansion could be made to follow a constant-entropy path by transferring heat from the process to counterbalance exactly the increase in entropy from irreversibilities. However, the probability of encountering such a process is remote; hence, *the words constant entropy and isentropic and the exponent k will be used to denote only reversible processes*

The work of an isentropic process can be determined from the polytropic equations (8-12) and (8-13) by substituting  $k$  for  $n$ . Similar substitutions can be made in Eqs (8-10) and (8-11) to find relationships between temperature, volume, and pressure for the isentropic process.

In the general case for the perfect gas the heat capacity is not a constant but is a function of temperature. The path equation for the isentropic process with variable heat capacities can be found from Eq (8-3) or (8-4) by substituting the variable-heat-capacity relationships. Thus, from Table IIB (Appendix) the general form of  $c_v$  is

$$c_v = A + \frac{B}{T} + \frac{C}{T^2}$$

When this value is substituted in Eq (8-3),

$$\left(\frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3}\right) dT + R \frac{dv}{v} = 0$$

This integrates to

$$A \ln \frac{T_2}{T_1} - B \left( \frac{1}{T_2} - \frac{1}{T_1} \right) - \frac{C}{2} \left( \frac{1}{T_2^2} - \frac{1}{T_1^2} \right) + R \ln \frac{v_2}{v_1} = 0 \quad (8-18)$$

Solution of this equation for  $T_2$  can be best made by trial

**Example 9.** In a steady-flow reversible process air enters the system at 440 F and 100 psia and leaves with pressure of 10 psia. The process is adiabatic. What is the change in kinetic energy if the system does work of amount 50 Btu lb<sub>m</sub><sup>-1</sup> of air?

**Solution:** For the isentropic process, Eq (8-13) is applicable with  $k$  substituted for  $n$ .

$$W_{\text{rev}} = \frac{kRT_1}{1-k} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - 1 \right] - \Delta \text{KE} = 0$$

Values for  $k$  could be selected from Table VI (Appendix), however, Fig 1A (Appendix) enables a mean value of  $k = 1.38$  to be selected for a more exact solution

$$\Delta \text{KE} = - \frac{1.38(1.986)900}{(0.38)29} (0.1^{0.2755} - 1) - 50 \frac{\text{Btu}}{\text{lb}_m}$$

Note that the units are determined by the gas constant  $R$ , and these units are desired to be Btu lb<sub>m</sub><sup>-1</sup> or

$$\Delta \text{KE} = 104 - 50 = 54 \text{ Btu/lb}_m \quad \text{Ans}$$

**8-7. Summary of Processes for the Perfect Gas.** Comparison of the processes for the perfect gas can be made by observing the relation-

ships between the paths of these processes on the  $Ts$  and  $pv$  diagrams (Fig 8-2). In reproducing Fig. 8-2 it will be found convenient to draw first the constant-pressure process for which  $n$  is zero. Then, the other curves can be drawn, noting that  $n$  increases from zero to infinity in the clockwise direction. Inspection of Fig 8-2 shows that  $n$  may have negative values. For a polytropic process with a negative number

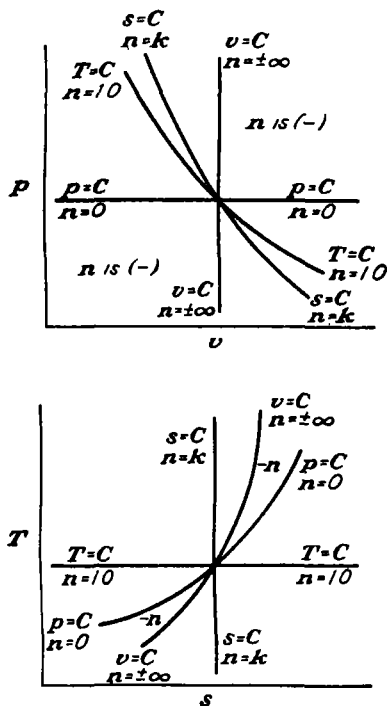


FIG 8-2 Process paths on  $pv$  and  $Ts$  diagrams

for the exponent  $n$ , Fig 8-2 reveals that pressure and specific volume will both increase (or both decrease) during the process. This will occur if energy is transferred to an expansion process at such a rate that the pressure rises instead of falling. (Essentially this occurs in an internal-combustion engine at the start of the power stroke when chemical energy is liberated.) Similarly, for a hypothetical compression process energy is taken away at a rate to cause the pressure to fall even though the volume is being decreased.

### 8-8. The Irreversible Process.

For an irreversible process the value for  $n$  cannot be used to compute either heat or work, but the process may still be represented in many cases on the  $pv$  or  $Ts$  diagram. The irreversible adiabatic process is often encountered. For this process the value of  $n$  will assume values dictated

<sup>1</sup> In a flow process with high initial kinetic energy even this value could be lessened, but, practically, such cases are rarely encountered.

perfect gas For the adiabatic compression process  $n$  is always greater than  $k$  with no limiting value because there is no limit to the amount of work that can be added to the system. Accordingly, the effect of irreversibilities is to cause  $n$  to *decrease* from the value for the reversible *expansion* process and to *increase* from the value for the reversible *compression* process (These same trends will be evident for all irreversible processes)

Although the transfers of heat and work for the irreversible process cannot be computed by evaluating the  $\int Tds$  and the  $\int p dv$ , such transfers can always be measured by changes in the surroundings that are evaluated by the First Law Consider an irreversible steady-flow process, for this process

$$Q - W = \Delta e_{\text{flow}} = h_2 - h_1 + \Delta \text{KE} \quad (3-13b)$$

and  $\Delta h$  and  $\Delta \text{KE}$  are evaluated at the boundary. Hence, the First Law analysis can be made for any process without regard for irreversibilities that may be present within the system, because all energy terms are measured at the boundary of the system<sup>1</sup>

For the perfect gas, Eq (7-8) can be substituted in Eq (3-13b)

$$[Q - W]_{\text{rev or irrev}} = c_p(T_2 - T_1) + \Delta \text{KE} \quad (8-19)$$

or

$$[Q - W]_{\text{rev or irrev}} = c_p T_1 \left( \frac{T_2}{T_1} - 1 \right) + \Delta \text{KE} \quad (8-20)$$

In Eq (8-20) it is permissible to substitute Eq (8-11):

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}}$$

for Eq (8-11) or (8-10) can be used to relate the boundary or end states of the irreversible process (although the value of  $n$  for the end states does not necessarily delineate the *path* because  $n$  need not be a constant throughout the irreversible process). In other words, if the boundary states for the irreversible process are known, it is always possible to find a value for  $n$  that will satisfy Eq. (8-11) Such a procedure does not require the same relationship between temperature and pressure to be maintained throughout the process, for this First Law derivation is based entirely on the properties at the boundary of the system Equation (8-11) can then be substituted in Eq (8-20)

<sup>1</sup> Note that Chap III on the First Law preceded the study of irreversible processes

$$[Q - W]_{\text{rev or irrev}} = c_p T_1 \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] + \Delta \text{KE} \quad (8-21)$$

and further substitution of Eq (7-11) results in

$$[Q - W]_{\text{rev or irrev}} = \frac{kRT_1}{k-1} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] + \Delta \text{KE} \quad (8-22)$$

The adiabatic work of the reversible or irreversible steady-flow process can be found by Eq (8-22) (i.e., when  $Q = 0$ ) although, of course, if the adiabatic process is reversible, Eq (8-22) becomes identical with Eq (8-13). Note again, however, that Eq (8-13) was derived entirely from path relationships while Eq (8-22) is merely the First Law dressed in perfect-gas relationships.

**Example 10:** Repeat Example 9, assuming that the adiabatic process is irreversible with the boundary states related by a value of  $n$  equal to 1.3

**Solution:** Equation (8-21) is simple to use and with  $Q = 0$ ,

$$\Delta \text{KE} = -c_p T_1 \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] - W$$

From Fig 1A (Appendix) an average value of  $c_p$  for the range of temperatures to be encountered is about  $c_p = 0.245 \text{ Btu R}^{-1} \text{ lb}_m^{-1}$ . Substituting this value,

$$\begin{aligned} \Delta \text{KE} &= -0.245(900) \left[ \left( \frac{1}{10} \right)^{0.231} - 1 \right] - 50 \\ &= 91.2 - 50 \\ &= 41.2 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

## 8-9. The Compression and Expansion of Gases Such as Air.

*a. The Ideal Compression Process (Steady-flow)* The compression of gases is an industrial problem of frequent occurrence. In Chap III, various types of compressors were discussed, and energy balances were made to account for the work that must be supplied. Now the problem is to select the best process for the compression, and the best process is one that requires a minimum of work. The  $pv$  diagram will be used to illustrate the work quantities required by different processes. For example, in Fig 8-3a the isothermal and isentropic compression processes are shown starting from the same initial state and proceeding over the same pressure ratio ( $p_2/p_1 = p_3/p_1$ ). Since most engineering machines use a steady-flow process, the reversible work is evaluated by the  $-\int v dp$  (if kinetic effects are negligible). Inspection of Fig 8-3a shows that the  $-\int v dp$  will decrease as the exponent  $n$  decreases; that is, less work is required when the gas is cooled during the compression process. However, if state 1 is at atmospheric temperature, the maximum cooling that can be attained without using a refrigerator

(and a refrigerator would require an additional source of work) is the isothermal process. Hence, the isothermal process is the ideal<sup>1</sup> flow process for compressing fluids because the minimum amount of work is required (area 1'122' is less than area 1'133'). Figure 8-3b shows that isothermal expansion will deliver more work than isentropic expansion if the fluid in both processes is at the same initial state.

It has already been demonstrated that the amount of work required to compress a fluid can be determined without inquiring into the mechanism of the compressor. If the reversible compression (or

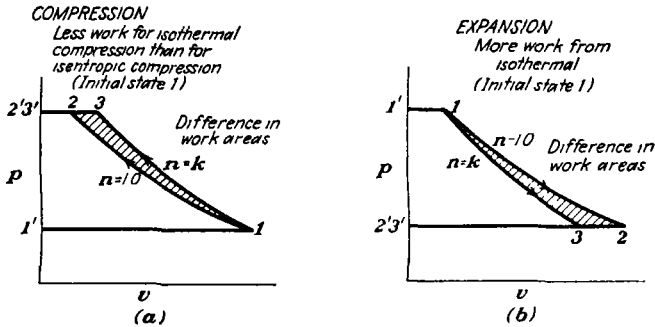


FIG 8-3 Comparison of isothermal and isentropic steady-flow processes of compression and expansion

expansion) is isothermal, Eq (8-7b) and Example 6 show that, for gases such as air,

$$W_{\text{rev steady flow isothermal}} = RT \ln \frac{p_1}{p_2} - \Delta KE \quad (8-7b)$$

while for polytropic (and isentropic) compression (or expansion) Art 8-5 shows that

$$W_{\text{rev steady flow polytropic}} = \frac{nRT_1}{1-n} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] - \Delta KE \quad (8-13)$$

Inspection of these equations reveals that the work depends not only upon the pressure ratio but also upon the initial temperature: the lower the initial temperature of the air, the less will be the work required for the compression.

<sup>1</sup> Although the ability of the compressed fluid to do expansion work is reduced by the cooling (area 2'211' is less than area 2'311'), yet in most practical cases this is not a loss. For either the compressed fluid is stored, or else it is transferred through pipes to other locations before use, and during this time the fluid is unavoidably cooled to the temperature of the surroundings.



*b The Actual Compression Process* In industry, large quantities of air (for example) must be compressed, and the compressor must be driven at high speed to supply the quantity of air demanded by a process. For this reason it is difficult to cool the fluid at a fast enough rate to maintain constant temperature. Therefore, the compression process in commercial machines approaches isentropic rather than the more desirable isothermal compression. In water-cooled, reciprocating-piston air compressors the polytropic exponent for the relationship  $pv^n = C$  will have a value from 1.25 to 1.35. In centrifugal blowers, without cooling, values of  $n$  above 1.4 are quite usual. It is best to use these values of  $n$  in the general equation (8-21) or (8-22), since the real

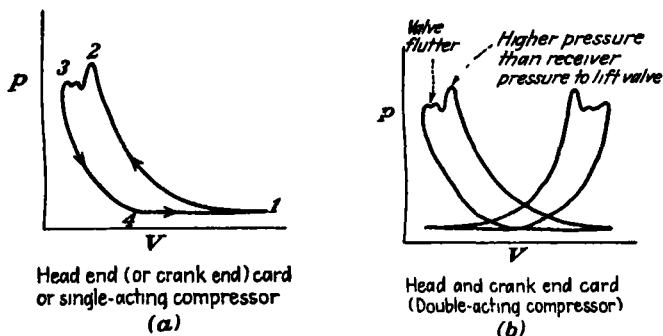


FIG 8-4 Indicator cards for reciprocating-piston compressor

compression is an irreversible process and values of  $n$  are usually determined from boundary conditions.

In some instances, water is injected into the air as a means of decreasing the work of compression. The saving in work arises from the high latent heat of the liquid, when vaporization of the water takes place, a reduction in temperature and therefore pressure of the air is obtained even though the vaporized water will contribute some part of the total pressure of the final mixture. This practice, however, must be used with care, since the presence of water may add to corrosion and erosion difficulties.

*c. The Indicator Card.* An indicator diagram (Art. 4-5) is used to show the events that occur in the piston-type compressor (Art. 3-6b). In Fig. 8-4, note that the card is similar in appearance to the  $pv$  diagram except that here the abscissa is volume. Compression of air (for example) occurs in the process 1-2; at 2 the receiver valve opens when the pressure in the cylinder is slightly greater than the pressure in the receiver. The compressed air is then pushed into the receiver, as

shown by the displacement path 2-3, until the piston reaches the end of its stroke (3). This point is not at zero volume because of the *clearance* that must be allowed in the actual mechanism (Art 3-6b) Now when the piston starts back on the return stroke, air cannot enter until the pressure is reduced to, or slightly below, the suction pressure. The air trapped in the clearance thus expands in process 3-4. At 4 the inlet valve opens and a new charge of air is drawn into the cylinder as shown by the displacement path 4-1, although the volume of air inducted is less than the piston displacement volume ( $V_D$ )

Note that this indicator diagram does not represent a thermodynamic cycle of processes because no change occurs in the state of the fluid along the constant-pressure (and variable-mass) paths 2-3 and 4-1. Here the fluid is merely displaced by the piston, and, because of this, the mass of fluid in the compressor will vary. In process 1-2 a mass of fluid is compressed to the receiver pressure, in the displacement 2-3 a portion of the mass is pushed into the receiver, in process 3-4 the residual mass of fluid in the clearance volume is expanded to the suction pressure; and along path 4-1 a new charge of fluid enters the cylinder. Notwithstanding this variation in mass, the enclosed area on the indicator card is proportional to the work because this area is a measure of the work done by the face of the piston in overcoming a force through a distance (Art 4-5). Hence, the indicator card is the usual method of obtaining the indicated work of the real engine. The work thus obtained is not for a cycle of processes undergone by the fluid but, rather, for a sequence of events undergone by the mechanism. (This sequence of events will be regularly repeated, and therefore it is a *mechanical cycle* of the engine and not a *thermodynamic cycle* of the fluid.)

The indicated mean effective pressure and the indicated work can be found for the mechanical cycle of the compressor in the same manner as for a thermodynamic cycle (Art 4-5)

$$p_{im} = imep = \frac{\text{closed area of diagram}}{\text{length of base}} \times \text{spring scale}$$

On one indicator card

$$W_{ind} = p_{im}AL = p_{im}V_D \quad (8-23)$$

where  $A$  = area of piston

$L$  = length of stroke

$V_D$  = piston displacement

The *indicated horse power* is defined as

$$\text{ihp} = \frac{p_{im} L A N}{33,000} \quad (8-24)$$

where  $N$  = number of cycles per minute [if one cylinder and single-acting piston,  $N$  = rpm; if  $x$  cylinders and double-acting piston,  $N = 2x(\text{rpm})$ ]

The *indicated horsepower* is numerically less than the *shaft horsepower* because of the power that must be spent to overcome friction, the *friction horsepower*.

A *conventional card* can be drawn by idealizing each event. In

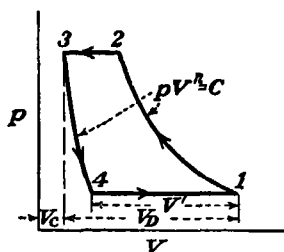


FIG 8-5 Conventional (reversible) indicator diagram

Fig 8-5 all events are specified to be reversible, and therefore the polytropic processes 1-2 and 3-4 must have identical<sup>1</sup> values of  $n$ . Although the work can be determined by Eq (8-13) [or Eq (8-7b) for the isothermal process], it will be of interest to obtain the same answer by evaluating areas on the indicator card

$$W_{\text{rev}} = \int_1^2 p dV + \int_2^3 p dV + \int_3^4 p dV + \int_4^1 p dV$$

and for reversible processes where  $p v^n = C'$  (and therefore  $p V^n = C'$ ) Eq (8-12) shows that

$$m_1 \int_1^2 p dv = \frac{m_1(p_2 v_2 - p_1 v_1)}{1 - n}$$

$$m_3 \int_3^4 p dv = \frac{m_3(p_4 v_4 - p_3 v_3)}{1 - n}$$

The displacement work at constant pressure (and variable mass) is

$$\int_2^3 p dV = p_3 V_3 - p_2 V_2 = m_3 p_3 v_3 - m_2 p_2 v_2$$

$$\int_4^1 p dV = p_1 V_1 - p_4 V_4 = m_1 p_1 v_1 - m_4 p_4 v_4$$

Hence,

$$W_{\text{rev}} = \frac{m_1(p_2 v_2 - p_1 v_1)}{1 - n} + \frac{m_3(p_4 v_4 - p_3 v_3)}{1 - n} + m_3 p_3 v_3 - m_2 p_2 v_2 + m_1 p_1 v_1 - m_4 p_4 v_4$$

which reduces to

$$W_{\text{rev}} = \frac{-n(m_3 p_3 v_3 + m_2 p_2 v_2 - m_1 p_1 v_1 + m_4 p_4 v_4)}{1 - n}$$

<sup>1</sup> If the exponents were not the same, then the temperature of the expanded fluid at 4 would not be equal to the temperature of the incoming fluid, and an irreversible mixing process would occur.

Since

$$m_1 = m_2 \text{ and } m_3 = m_4 \text{ while } p_2 = p_3 \text{ and } p_1 = p_4$$

and the fluid is unchanged in state during the displacement strokes 2-3 and also 4-1, then

$$v_1 = v_4 \quad v_2 = v_3$$

Therefore,

$$W_{\text{rev}} = \frac{-n(m_3 - m_1)(p_2 v_2 - p_1 v_1)}{1 - n}$$

and thus Eq (8-13) is again obtained

$$W_{\text{rev}} = \frac{nm(p_2 v_2 - p_1 v_1)}{1 - n}$$

where  $m$  = mass of fluid entering or leaving the compressor  
 $= (m_1 - m_2)$

Since Eq (8-13) was originally derived (Art 8-5) without picturing the mechanism for the compressor, and since in this derivation the compressor has clearance, then it should be apparent that clearance has no effect on the work theoretically required to compress the fluid. Of course, in real machines the compression and reexpansion of a portion of the gas cause a loss because both processes are irreversible, hence, it is desirable to use low clearances. A usual value for the clearance volume in medium-pressure machines (100 psia) is 6 per cent of the piston displacement volume  $V_D$ . For higher pressures, smaller clearances are desirable and necessary. Note that the clearance volume controls the amount of fluid discharged, if the clearance volume is large and the receiver pressure is high, it is entirely possible that no fluid will be delivered by the compressor.

*d Volumetric Efficiency* If the entire displacement volume of the compressor could be filled with air at the same temperature and pressure that exist in the surroundings, then the maximum amount of compressed air would be delivered to the receiver. In the real machine, a lesser amount of air is delivered because the clearance prevents the displacement volume from being effectively used and, also, fluid friction losses will reduce the suction pressure. Because of these factors, the *volumetric efficiency* of the compressor (or of any positive displacement machine) is defined

$$\eta_v = \text{volumetric efficiency} = \frac{m}{m_D} \quad (8-25)$$

$m$  = mass of fluid inducted or delivered per stroke  
 $m_D$  = theoretical mass of fluid to fill the piston displacement volume under optimum (usually atmospheric) conditions of pressure and temperature

Although the volumetric efficiency is a mass ratio, it is usually determined by measuring volumes

$$\eta_v = \frac{\text{compressor capacity (cfm)}}{\text{compressor displacement (cfm)}} \bigg]_{p,T} = \frac{C}{D} \bigg]_{p,T} \quad (8-26)$$

The *compressor displacement* ( $D$ ) is the total volume swept by the pistons in 1 minute (A double-acting piston will displace a volume twice that of a single-acting piston) The *capacity* ( $C$ ) of the compressor is defined to be the volume of gas delivered as measured in cubic feet per minute (cfm) for the conditions of temperature and pressure existing in the inlet surroundings (and not in the receiver) For an air compressor, the atmosphere is the surroundings, and the volume of air delivered by the compressor, when measured at atmospheric pressure, temperature, and humidity is called *free air*

A *conventional volumetric efficiency* can be determined from the conventional card, and this efficiency represents the optimum value for the real compressor In Fig 8-5, since the same temperature and pressure exist at any point along path 4-1, then

$$\eta_{v_{\text{conv}}} = \frac{m}{m_D} = \frac{V_1 - V_4}{V_D} = \frac{V'}{V_D} \quad (8-27)$$

The *clearance* is defined as the fraction

$$c = \frac{V_3}{V_D} \quad (8-28)$$

and by inspection of Fig 8-5

$$V_1 = V_3 + V_D$$

Substituting Eq (8-28),

$$V_1 = cV_D + V_D = V_D(c + 1) \quad (a)$$

Since

$$V_4 = V_3 \left( \frac{p_3}{p_4} \right)^{\frac{1}{n}} = cV_D \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}} \quad (b)$$

then,

$$\begin{aligned} \eta_{v_{\text{conv}}} &= \frac{V_1 - V_4}{V_D} = \frac{V_D + cV_D - cV_D (p_2/p_1)^{\frac{1}{n}}}{V_D} \\ \eta_{v_{\text{conv}}} &= 1 + c - c \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}} \end{aligned} \quad (8-29)$$

**Example 11:** Determine the heat transferred in a reversible compressor during the compression and expansion processes if  $n = 1.30$ , the final pressure is 125 psia,

the clearance is 4 per cent, and the fluid is air at  $p = 14.7$  psia and  $t = 60$  F (Data are similar to those in Example 8)

**Solution:** The amount of heat transferred during each process of the compressor depends on the mass of air in the cylinder. The calculations are based upon unit mass delivered by the compressor

$$m = 1 \text{ lb}_m$$

Then, by Eq (8-27)

$$m_D = \frac{m}{\eta_v}$$

By Eq (a)

$$V_1 = V_D(c + 1)$$

Therefore,

$$m_{1 \text{ or } 2} = m_D(c + 1)$$

And by definition

$$\text{Mass in clearance} = (\text{mass in cylinder}) - (\text{mass delivered})$$

$$m_{3 \text{ or } 4} = m_{1 \text{ or } 2} - m$$

To evaluate the relative masses, the conventional volumetric efficiency is calculated

$$\begin{aligned} \eta_v &= 1 + c - c \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}} \\ &= 1 + 0.04 - 0.04 \left( \frac{125}{14.7} \right)^{0.77} = 0.83 \end{aligned} \quad (8-29)$$

Hence,

$$\begin{aligned} m &= 1 \text{ lb}_m \\ m_D &= \frac{m}{\eta_v} = \frac{1}{0.83} = 1.20 \text{ lb}_m/\text{lb}_m \text{ delivered} \\ m_{1 \text{ or } 2} &= m_D(c + 1) = 1.2(1.04) = 1.25 \text{ lb}_m/\text{lb}_m \text{ delivered} \\ m_{3 \text{ or } 4} &= m_{1 \text{ or } 2} - m = 1.25 - 1.0 = 0.25 \text{ lb}_m/\text{lb}_m \text{ delivered} \end{aligned}$$

The heat *rejected* to the cooling water on the compression stroke 1-2 is (data from Example 8)

$$\begin{aligned} Q_{1-2} &= m_1 c_v \left( \frac{k-n}{1-n} \right) (T_2 - T_1) \\ &= 1.25(0.171) \left( \frac{1.4-1.3}{1-1.3} \right) (853 - 520) \\ &= -23.75 \text{ Btu/lb}_m \text{ delivered} \quad \text{Ans} \end{aligned}$$

The heat *added* to the cooling water on the expansion stroke 3-4 is

$$\begin{aligned} Q_{3-4} &= m_3 c_v \left( \frac{k-n}{1-n} \right) (T_4 - T_3) \\ &= 4.75 \text{ Btu/lb}_m \text{ delivered} \quad \text{Ans} \end{aligned}$$

The net heat transfer to the cooling water is

$$\begin{aligned} \Sigma Q &= Q_{1-2} + Q_{3-4} \\ &= -23.75 + 4.75 = -19.0 \text{ Btu/lb}_m \text{ delivered} \quad \text{Ans} \end{aligned}$$

and this checks the answer found in Example 8

*e Multistage Compression* The work required to compress a gas is controlled by three factors (1) the compression process, (2) the pressure ratio, and (3) the initial temperature of the gas, although these factors cannot be readily varied. Any selection of the compression process is restricted by the mass flow rate, and therefore isothermal compression, while most desirable, is also most impractical. The pressure ratio cannot be changed because it is fixed by the process demands for the compressed fluid. However, the third factor, the initial temperature of the gas, can be lowered to effect a saving in work.

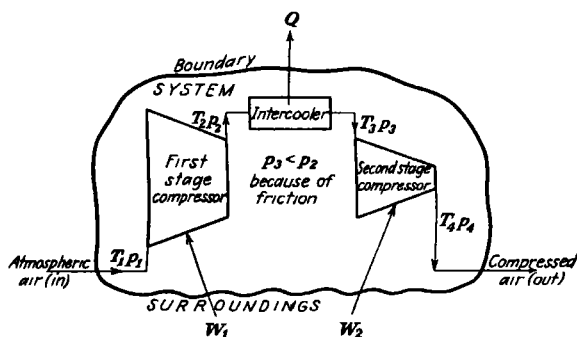


FIG 8-6 System of two compressors and intercooler (multistage or series compression)

In the case of an air compressor, the inlet air is at atmospheric temperature, and therefore this temperature cannot be reduced by using lake or river water, which is the cheapest coolant, because the water would be at essentially the same temperature as the air. But, instead of using one compressor, suppose that two compressors are connected in series. This series combination will theoretically require the same amount of work as the single compressor, and, practically, it will require slightly more work owing to the increased friction caused by the more complex mechanism. However, the compressed air leaving the first compressor (the first stage) will be at a high temperature relative to the temperature of the available cooling water, and therefore effective cooling of the air is readily accomplished by an intercooler (Fig 8-6). Thus, the air entering the second compressor (the second stage) is reduced in temperature, and for this reason less work will be required by the multistage compressor than if a single compressor had been used.

The work required for a real multistage compressor is readily evaluated by the First Law equation (8-22) applied to the system of two compressors and intercooler (Fig 8-6). For the reversible com-

pressor, the ideal relationship, Eq (8-13) can be applied, in turn, to each compressor

$$W_{\text{rev multistage}} = \frac{nmRT_1}{1-n} \left[ \left( \frac{p_1}{p_i} \right)^{\frac{n-1}{n}} - 1 \right] + \frac{nmRT_3}{1-n} \left[ \left( \frac{p_4}{p_i} \right)^{\frac{n-1}{n}} - 1 \right] \quad (8-30a)$$

Here it is assumed that the compression exponent is the same for both machines and that the outlet pressure ( $p_i$ ) for the first compressor is equal to the inlet pressure for the second compressor ( $p_1 = p_2 = p_3$  in Fig 8-6) The latter assumption is equivalent to stating that no pressure drop occurs in the intercooler If the intercooling is *ideal* or *perfect*, no pressure drop will occur, and, also, the outlet temperature of the air  $T_3$  will be reduced to  $T_1$

Since the work of the multistage compressor is governed by the intermediate pressure  $p_i$ , the value of  $p_i$  for minimum work is of interest Upon differentiating Eq (8-30a) with respect to  $p_i$  and setting the derivative equal to zero,

$$\left. \frac{dW}{dp_i} \right]_{T_1=T_3} = 0$$

it is found that

$$p_i = (p_1 p_4)^{\frac{1}{2}} \quad (8-31)$$

and therefore

$$\frac{p_1}{p_i} = \frac{p_4}{p_i}$$

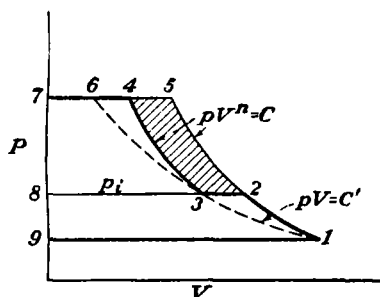


FIG 8-7 Savings in work from two-stage compression with intercooler

Thus, the minimum work for ideal two-stage compression is obtained when the low-pressure stage has the same pressure ratio as the high-pressure stage With this division of the pressure ratio, each compressor will require the same amount of work because the inlet air temperature is the same for either stage

$$W = \frac{2mnRT_1}{1-n} \left[ \left( \frac{p_1}{p_i} \right)^{\frac{n-1}{n}} - 1 \right] \quad (8-30b)$$

The work saved by multistage compression can be best illustrated by the  $pV$  diagram (Fig 8-7) (Since clearance does not affect the theoretical work, Fig 8-7 is drawn for a compressor without clearance) If the compression were single stage, the path for the polytropic compression process would be 1-5 and the work would be proportional to area 1579 If the compression were isothermal and single stage, the work would be proportional to area 1679 With multistage and poly-



tropic compression, the work for the first stage is represented by area 1289, and the work for the second stage by area 3478. Thus, the work saved by two-stage polytropic compression, relative to single-stage polytropic compression, is proportional to the area 2345.

**Example 12:** A two-stage, double-acting air compressor is constructed with the same stroke for both the high- and low-pressure cylinders. Air is to be compressed from atmospheric pressure to 200 psia. If the capacity is to be 400 cfm, determine the diameter of the cylinders and the amount of heat that must be transferred in the intercooler. (Neglect possible losses.)

$$\begin{aligned}\text{Stroke} &= 14 \text{ in} & n &= 1.3 & \text{rpm} &= 130 & p_a &= 14.7 & t_a &= 80^\circ \text{F} \\ c &= 0.03, \text{ or } 3 \text{ per cent}\end{aligned}$$

**Solution:** The volumetric efficiency is

$$\eta_v = 1 + c - c \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}}$$

and

$$p_1 = (p_1 p_2)^{\frac{1}{2}} = [(14.7)(200)]^{\frac{1}{2}} = 54.3 \text{ psia}$$

$$\begin{aligned}\eta_v &= 1 + 0.03 - 0.03(3.69)^{\frac{1}{1.3}} \\ &= 0.948, \text{ or } 94.8 \text{ per cent}\end{aligned}$$

Since

$$\eta_v = \frac{\text{capacity}}{\text{compressor displacement}} = \frac{400 \text{ cfm}}{D}$$

then the compressor displacement of the low-pressure stage is

$$D_L = \frac{400}{0.948} = 422 \text{ cfm}$$

and the piston (double-acting) displacement can be found from

$$\begin{aligned}V_{DL}(\text{rpm})(2) &= D_L \\ V_{DL} &= \frac{422}{2(130)} = 1.62 \text{ ft}^3\end{aligned}$$

Hence, the diameter of the low-pressure stage is

$$\begin{aligned}\frac{\pi}{4} d_L^2 (14) &= 1.62(1,728) \\ d_L &= 16 \text{ in} \quad \text{Ans}\end{aligned}$$

The volume of air entering the second stage is (at  $p_1 = 54.3$  psia and  $t_1 = 80^\circ \text{F}$ )

$$\begin{aligned}\frac{V'_L}{V'_H} &= \frac{p_1}{p_2} \\ V'_H &= V'_L \frac{p_1}{p_2} = 400 \left( \frac{14.7}{54.3} \right) = 108 \text{ cfm}\end{aligned}$$

and as before

$$\begin{aligned} D_H &= \frac{108}{0.948} = 114 \text{ cfm} \\ V_{DH} &= 0.44 \text{ ft}^3 \\ d_H &= 8.32 \text{ in} \quad \text{Ans} \end{aligned}$$

The mass flow rate of air is

$$m = \frac{pV}{RT} = \frac{14.7(144)(400)}{53.3(540)} = 29.4 \text{ lb}_m/\text{min}$$

The temperature of the air entering the intercooler is

$$\begin{aligned} T_2 &= T_1 \left( \frac{p_1}{p_2} \right)^{\frac{n-1}{n}} = 540(3.69)^{0.231} \\ &= 730 \text{ R} \end{aligned}$$

The heat transferred in the intercooler to reduce the temperature of the air to  $T_1 = T_3$  is

$$\begin{aligned} Q &= mc_p(T_3 - T_2) \\ &= 29.4(0.24)(730 - 540) \\ &= 1340 \text{ Btu/min} \quad \text{Ans.} \end{aligned}$$

*f Compressor Efficiencies* The simplicity of the electric motor makes it an ideal driver for the compressor. However, for portable compressors, or for locations where electric energy is either too expensive or else not available, gasoline or diesel engines and steam turbines or engines are used as the *prime mover*. Because of these different types of prime movers, the efficiency of the compressor is defined in different manners.

The *mechanical efficiency* is best defined

$$\eta_m = \frac{\text{indicated work (or power) of the compressor}}{\text{shaft work (or power) supplied}} \quad (8-32)$$

However, many large compressors are built as an integral part of a reciprocating engine and for such cases

$$\eta_m = \frac{\text{indicated work (or power) of the compressor}}{\text{indicated work (or power) of the prime mover}} \quad (8-33)$$

The mechanical efficiency of commercial air compressors ranges from about 90 per cent for small machines to 97 per cent for the larger compressors.

The *compression efficiency* is based upon either ideal isothermal or ideal isentropic compression. Thus, the *isentropic*<sup>1</sup> *compression efficiency*

<sup>1</sup> This term is more often called, unfortunately, the *adiabatic* compression efficiency.

ciency is defined

$$\eta_{c_{\text{isen}}} = \frac{\text{work (or power) required for isentropic compression}}{\text{indicated work (or power) of the compressor}} \quad (8-34)$$

And the *isothermal compression efficiency* is defined

$$\eta_{c_{\text{isoth}}} = \frac{\text{work (or power) required for isothermal compression}}{\text{indicated work (or power) of the compressor}} \quad (8-35)$$

Typical values of these efficiencies for a commercial machine are 74 per cent (isothermal efficiency) and 84 per cent (isentropic efficiency)

For the multistage compressor with intercooler the isentropic compression efficiency is defined

$$\eta_{c_{\text{ms}}} = \frac{\text{work (or power) for isentropic compression, ideal intercooling}}{\text{indicated work (or power) of the compressors}} \quad (8-36)$$

The *over-all efficiency* is the product of the mechanical and the compression efficiencies. Thus, the over-all efficiency may be given as the *isentropic over-all efficiency* or as the *isothermal over-all efficiency*

**8-10. Air Tables.** The compression and expansion of air occurs in many problems in engineering. Solution of equations in the form of Eq (8-18) is tedious, consequently, the properties of air have been compiled<sup>1</sup> in a manner designed to facilitate such computations. Although the data are treated on the assumption that air is a perfect gas, inspection of Fig 1A (Appendix) shows that this assumption is quite accurate for the range of pressures and temperatures usually encountered in engineering processes.

The Air Table<sup>1</sup> plots values for enthalpy  $h$ , internal energy  $u$ , relative pressure  $p_r$ , relative volume  $v_r$ , and  $\phi$ , against temperature, as the only independent variable, for the range 300 to 6500 R. The form of the Air Table is illustrated by Table 8-1. At a temperature of 400 R note that

$$h = 0 \quad p_r = 1.0 \quad v_r = 10,000 \quad \phi = 0$$

The new terms *relative pressure*  $p_r$ , *relative volume*  $v_r$ , and  $\phi$  will be shown to be functions only of temperature, and, later, the utility for these terms will be demonstrated by several examples.

<sup>1</sup> KEENAN, J. H. and J. KAYE "Thermodynamic Properties of Air," John Wiley & Sons, New York, 1945

TABLE 8-1—AIR AT LOW PRESSURES

$T$	$t$	$h$	$p_r$	$u$	$v_r$	$\phi$
330	-129 7	-16 77	5105	-39 39	16159	- 04609
400	- 59 7	0	1 0000	-27 42	10000	0
468	8 3	16 30	1 7315	-15 78	6757	03762
520	60 3	28 77	2 504	- 6 87	5192	06290
528	68 3	30 69	2 641	- 5 50	4998	06657
560	100 3	38 38	3 246	- 0 01	4313	08070
600	140 3	48 00	4 135	6 87	3628	09729
700	240 3	72 11	7 112	24 13	2461	13447
800	340 3	96 38	11 410	41 55	1752 9	16687
900	440 3	120 86	17 374	59 17	1295	19569
996	536 3	144 60	25 045	76 33	994 2	22075
1000	540 3	145 59	25 41	77 05	983 8	22175
1050	590 3	158 07	30 35	86 10	864 8	23393
1200	740 3	195 96	49 64	113 71	604 3	26765
1510	1050 3	276 54	118 58	173 04	318 3	32734
1800	1340 3	354 50	236 1	231 12	190 59	37455
2000	1540 3	409 55	360 4	272 46	138 72	40354
3450	2990 3	828 72	3568 0	592 25	24 17	56067
4000	3540 3	993 61	6813 0	719 43	14 678	60500
5000	4540 3	1298 48	18373 0	955 75	6 803	67301
6000	5540 3	1608 16	41870 0	1196 90	3 583	72946

Abstracted, by permission, from J. Keenan and J. Kaye, "Thermodynamic Properties of Air," John Wiley & Sons, Inc., New York, 1945

The function  $\phi$  is defined

$$\phi = \int_{400 \text{ R}}^T c_p \frac{dT}{T} \text{ Btu/lb}_m \text{ R} \quad \text{and} \quad \phi = 0 \text{ at } 400 \text{ R} \quad (8-37a)$$

This equation shows that  $\phi$  is a function only of temperature. Values of  $\phi$  were computed from data similar to that of Table IIB (Appendix). Suppose that the change in entropy between two states is to be evaluated. Equation (8-4) shows that

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

$$\Delta s = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{p_2}{p_1}$$

and by Eq (8-37a)

$$\Delta s = \phi_2 - \phi_1 - R \ln \frac{p_2}{p_1} \quad (8-37b)$$

The values for  $\phi$  in the Air Table enable the change in entropy to be easily computed, and the labor of solving Eq (8-18) is avoided.

The *relative pressure* is defined

$$p_r = \left. \frac{p}{p_{400 \text{ R}}} \right]_{s=C} \quad (8-38a)$$

and thus  $p_r = 1$  at any pressure where the temperature is 400 R. That  $p_r$  is a function of temperature alone is shown by Eq (8-4)

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p} = 0 \quad \text{if } s = \text{constant}$$

or

$$\ln \frac{p_2}{p_1} \Big|_{s=C} = \frac{\phi_2 - \phi_1}{R}$$

and

$$\ln \frac{p}{p_{400 \text{ R}}} \Big|_{s=C} = \frac{\phi}{R} = \ln p_r$$

By means of this equation, values for  $p_r$  can be computed for each temperature in the Air Table. Equation (8-38a) is helpful in solving isentropic compression or expansion problems, between any two states at constant entropy

$$\frac{p_{r1}}{p_{r2}} = \frac{p_1/p_{400 \text{ R}} \Big|_{s=C}}{p_2/p_{400 \text{ R}} \Big|_{s=C}} = \frac{p_1}{p_2} \Big|_{s=C} \quad (8-38b)$$

The ratio of the relative pressures is equal to the isentropic pressure ratio. The relative volume is defined

$$v_r = \frac{10,000v}{v_{400 \text{ R}}} \Big|_{s=C} \quad (8-39a)$$

and thus  $v_r = 10,000$  at any volume where the temperature is 400 R. This term, like the others, is a function of temperature alone, as is evident by combining Eqs (8-38a) and (8-39a)

$$p_r v_r = \frac{p}{p_{400 \text{ R}}} \frac{10,000v}{v_{400 \text{ R}}} = \frac{10,000pv}{(pv)_{400 \text{ R}}} = \frac{10,000RT}{(RT)_{400 \text{ R}}}$$

and therefore

$$v_r = \frac{10,000T}{400p_r}$$

By means of this equation values of  $v_r$  can be computed. The relative volume, like the relative pressure, is useful in solving isentropic compression or expansion problems, between any two states at constant entropy

$$\frac{v_{r1}}{v_{r2}} = \frac{10,000v_1/v_{400} \Big|_{s=C}}{10,000v_2/v_{400} \Big|_{s=C}} = \frac{v_1}{v_2} \Big|_{s=C} \quad (8-39b)$$

The ratio of the relative volumes is equal to the isentropic compression or expansion ratio

**Example 13:** Repeat Example 10, taking into account the variation of heat capacity with temperature by use of the Air Table. (Note that in Example 10 the variation in heat capacity was compensated by use of an average value for  $c_p$ .)

**Solution:** Equation (3-13b) is the simplest equation

$$Q - W = h_2 - h_1 + \Delta KE \quad \text{and} \quad Q = 0$$

and

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{n-1}{n}}$$

$$T_2 = \frac{900}{10^{0.231}} = 528 \text{ R}$$

Values for  $h_1$  and  $h_2$  can be selected from the Air Table for temperatures of 900 and 528 R

$$h_1 = 120.86$$

$$h_2 = 30.69$$

$$-\Delta h = 90.17 \text{ Btu/lb}_m$$

Hence,

$$\Delta KE = -\Delta h - W$$

$$= 90.17 - 50 = 40.17 \text{ Btu/lb}_m \quad \text{Ans}$$

Compare this with the answer for Example 10, 41.2 Btu/lb<sub>m</sub>. The answer could also be checked by the air chart, Fig IX, Appendix

**Example 14:** Repeat Example 9, using the Air Table

**Solution:** The data are repeated

$$T_1 = 900 \text{ R} \quad T_2 = \text{unknown}$$

$$p_1 = 100 \text{ psia} \quad p_2 = 10 \text{ psia}$$

$$W_{\text{rev}} = 50 \text{ Btu/lb}_m$$

The data from the Air Table for  $T_1 = 900 \text{ R}$  are

$$h_1 = 120.86 \text{ Btu/lb}_m$$

$$p_{r1} = 17.374$$

Using Eq (8-38b),

$$\frac{p_{r2}}{p_{r1}} = \frac{p_2}{p_1}$$

$$p_{r2} = p_{r1} \frac{p_2}{p_1} = 17.374 \left(\frac{1}{10}\right) = 1.7374$$

With this value of  $p_r$  enter the Table and find

$$T_2 = 468 \text{ R}$$

$$h_2 = 16.3 \text{ Btu/lb}_m$$

When these values are substituted in the First Law equation,

$$\Delta KE = h_1 - h_2 - W$$

$$= 120.86 - 16.3 - 50$$

$$= 54.56 \text{ Btu/lb}_m \quad \text{Ans}$$

Compare this with the answer for Example 9, 54.0 Btu/lb<sub>m</sub>.

**Example 15:** Determine the change in entropy for the process of Examples 10 and 13 by computations based upon the Air Table

**Solution:** For an isentropic expansion from  $T_1 = 900 \text{ R}$ ,

$$p_1 = 100 \text{ psi, to } p_2 = 10 \text{ psia}$$

$$T_2 = 468 \text{ R} \quad (\text{Example 14})$$

For the irreversible expansion from the same initial state

$$T_2 = 528 \text{ R} \quad (\text{Example 13})$$

Both of these values are at the same pressure, hence, by Eq (8-37b),

$$\Delta s = \Delta \phi$$

From the Air Table, •

$$\begin{aligned} \phi &= 0.06657 && \text{at } 528 \text{ R} \\ \phi &= 0.03762 && \text{at } 468 \text{ R} \\ \Delta s = \Delta \phi &= 0.02895 \text{ Btu/lb}_m \text{ R} && \text{Ans} \end{aligned}$$

An alternative solution is to find the change in entropy from the initial to final states

$$\begin{aligned} T_1 &= 900 \text{ R} && T_2 = 528 \text{ R} \\ p_1 &= 100 \text{ psia} && p_2 = 10 \text{ psia} \end{aligned}$$

From the Air Table for these temperatures,

$$\begin{aligned} \phi_1 &= 0.19569 \\ \phi_2 &= 0.06657 \\ \Delta \phi &= -0.12912 \end{aligned}$$

From Eq (8-37b),

$$\begin{aligned} \Delta s &= \phi_2 - \phi_1 - R \ln \frac{p_2}{p_1} \\ &= -0.12912 + \frac{1.986}{29} (2.3) \\ &= -0.12912 + 0.1575 = 0.02838 \text{ Btu/lb}_m \text{ R} \quad \text{Ans} \end{aligned}$$

**Example 16.** A pound of air is reversibly and adiabatically compressed in a nonflow process through a compression ratio (volume ratio) of 6 from an initial state of 14.7 psia and 60 F. What are the values for the final pressure and temperature, and how much work is required? (Note Fig IX in Appendix )

**Solution:** From the Air Table for  $T_1 = 520 \text{ R}$ ,

$$\begin{aligned} v_{r1} &= 5.192 \\ u_1 &= -6.87 \text{ Btu/lb}_m \\ p_{r1} &= 2.504 \end{aligned}$$

From Eq (8-39b),

$$\begin{aligned} \frac{v_{r1}}{v_{r2}} &= \frac{v_1}{v_2} \\ v_{r2} &= \frac{v_{r1}}{v_1/v_2} = \frac{5.192}{6} = 865.3 \end{aligned}$$

For this value of  $v_r$ , the Air Table shows that

$$\begin{aligned} T_2 &= 1050 \text{ R} && \text{Ans} \\ u &= 86.10 \text{ Btu/lb}_m \\ p_{r2} &= 30.35 \end{aligned}$$

Using Eq (8-38b),

$$\begin{aligned} \frac{p_{r1}}{p_{r2}} &= \frac{p_1}{p_2} \\ p_2 &= p_1 \frac{p_{r2}}{p_{r1}} = 14.7 \frac{30.35}{2.504} \\ &= 178 \text{ psia} && \text{Ans} \end{aligned}$$

while the work is equal to

$$Q - W = \Delta u$$

and, since  $Q = 0$ ,

$$\begin{aligned} W &= u_1 - u_2 \\ &= -6.87 - 86.10 \\ &= -92.97 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

For this range of temperatures the value of  $k$  from Fig. 1A (Appendix) is 1.39. With this value in Eqs. (8-17), (8-10), and (8-12),

$$\begin{aligned} p_2 &= p_1 \left( \frac{v_1}{v_2} \right)^k = 14.7(6)^{1.39} = 178 \text{ psia} \quad \text{Ans} \\ T_2 &= T_1 \left( \frac{v_1}{v_2} \right)^{k-1} = 520(6)^{0.39} = 1050 \text{ R} \quad \text{Ans} \\ W &= \frac{R(T_2 - T_1)}{1 - k} = -\frac{1.986(530)}{29(0.39)} = -93.1 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

### Problems

For the following problems

1. Gas constant values can be found in Table VI (Appendix)
2. Assume the process to be reversible unless otherwise implied but determine for each answer whether this assumption was necessary for solution
3. Answers to be Btu units and for work answers show also units of foot pound force. Mass unit is to be the pound mole or pound mass as implied by the statement of the problem. If in doubt, answers are to be expressed in both units
4. Heat-capacity values are assumed constant unless otherwise stated
5. All fluids are assumed to behave as perfect gases unless otherwise stated
6. Solutions can be checked by the air chart (Fig. IX, Appendix)

### NONFLOW CONSTANT-VOLUME PROCESSES

1. A tank contains 5 ft<sup>3</sup> of nitrogen at 200 psia and 200 F. The tank is cooled until the temperature of the nitrogen is 60 F. Determine the amount of heat transferred from the nitrogen, the final pressure, the change in entropy, and the change in enthalpy

2. Repeat Prob. 1, assuming that carbon dioxide is the fluid

3. Repeat Prob. 1, assuming that heat is transferred until the pressure reaches 20 psia. Determine the final temperature, change in entropy, and the amount of heat removed

4. A constant volume of air is cooled by transfer of 40 Btu of heat until the pressure is 30 psia. If the initial temperature is 300 F and the initial pressure is 100 psia, determine the final temperature, change in entropy, change in enthalpy, and the work done

5. Repeat Prob. 3, assuming that hydrogen is the fluid

6. Repeat Prob. 4, assuming that methane is the fluid

7. Three pounds of air confined in a closed tank are heated until the enthalpy is increased 40 Btu lb<sub>m</sub><sup>-1</sup>. If the initial pressure is 100 psia and the final temperature is 400 F, determine the change in internal energy

8. Repeat Prob. 7, assuming that the mass is 0.1 mole and the increase in enthalpy is 1100 Btu mole<sup>-1</sup>



9. Oxygen is confined in a tank under a pressure of 100 psia and at a temperature of 300 F. If this air is cooled until the entropy decreases by  $0.264 \text{ Btu lb}_m^{-1} \text{ R}^{-1}$ , what will be the final pressure?

10. Repeat Prob. 9, assuming that helium is the fluid while the entropy change is  $1.0 \text{ Btu mole}^{-1} \text{ R}^{-1}$ .

11. A pound of argon at 100 F and 25 psia is heated at constant volume until the pressure is 75 psia. Determine the heat transferred, change in enthalpy and entropy, and the final temperature.

#### NONFLOW CONSTANT-PRESSURE PROCESSES

12. A pound of air at 100 F and 20 psia is expanded at constant pressure until the entropy has changed by  $0.3 \text{ Btu lb}_m^{-1} \text{ R}^{-1}$ . Determine the final temperature, heat transferred, and change in enthalpy and internal energy.

13. Repeat Prob. 12, assuming that the fluid is argon of mass 0.4 mole while the entropy changes by  $12 \text{ Btu mole}^{-1} \text{ R}^{-1}$ .

14. Air at 100 F is heated at constant pressure until the volume doubles while the entropy increases  $0.25 \text{ Btu R}^{-1}$ . Compute the mass of air present.

15. A mole of air at 14.7 psia and 60 F is heated at constant pressure until the volume is tripled. Determine the work, change of internal energy, entropy, and amount of heat transferred.

16. Repeat Prob. 15, assuming that carbon dioxide is the fluid.

17. Nitrogen undergoes a constant-pressure process until the change in internal energy is 20 Btu and the final temperature is 300 F. How much heat was added, and how much work was done?

18. One pound of air undergoes a constant-pressure process wherein the temperature doubles while the internal energy increases by  $100 \text{ Btu lb}_m^{-1}$ . Find the heat and work transferred, change in entropy and enthalpy, and initial and final temperatures.

19. Repeat Prob. 18, assuming that 1 mole of hydrogen is the fluid while the internal energy increases  $100 \text{ Btu mole}^{-1}$ .

#### ISOTHERMAL PROCESS

20. A gas is compressed at constant temperature from 15 psia and  $25 \text{ ft}^3$  to 105 psia. Compute the work and heat transferred and the change in entropy, internal energy, and enthalpy. Repeat, assuming a flow process.

21. One mole of air at 75 F is isothermally compressed to 600 psia while the volume is halved. Compute the heat and work transferred, the change in entropy, and the initial pressure.

22. Repeat Prob. 21, assuming helium to be the fluid.

23. Air at 60 F is isothermally compressed to 200 psia while the volume is halved and the entropy decreases by  $-0.5 \text{ Btu R}^{-1}$ . Compute the initial volume, mass, heat, and work transferred.

24. Five cubic feet of air is isothermally expanded to a pressure of 20 psia from an initial pressure of 80 psia. Find the work and heat transferred and the change in entropy.

25. Two pounds of nitrogen at 20 psia with specific volume of  $10 \text{ ft}^3 \text{ lb}_m^{-1}$  are isothermally compressed to 100 psia. Compute the work and heat transferred, temperature, and change of entropy.

26. Repeat Prob. 25, assuming 0.1 mole of air to be the fluid with specific volume of  $300 \text{ ft}^3 \text{ mole}^{-1}$

27. Two pounds of methane are isothermally compressed at 60 F while 200 Btu of heat are transferred (a) Find the pressure and volume ratios of compression (b) If the final pressure is 80 psia, find the change in entropy and the original pressure

#### NONFLOW POLYTROPIC PROCESS

28. A pound of air is expanded in a polytropic process with  $n = 1.2$  from  $p_1 = 100 \text{ psia}$  and  $t_1 = 260 \text{ F}$  to  $t_2 = 60 \text{ F}$ . Find the heat and work transferred and the change in entropy, enthalpy, and internal energy

29. Repeat Prob. 28, assuming that 1.0 mole of hydrogen is the fluid

30. A pound of air is compressed in a polytropic process from  $p_1 = 20 \text{ psia}$  to  $p_2 = 100 \text{ psia}$  while the entropy increases by  $0.046 \text{ Btu lb}_m^{-1} \text{ R}^{-1}$ . Determine the value for  $n$

31. A pound of air is compressed from  $-55$  to  $75 \text{ F}$  while the volume is halved. Find the work and heat transferred per pound of air

32. A gas is expanded from a pressure of 100 to 10 psia with corresponding volume of  $2.3 \text{ ft}^3$  while work of amount 10 Btu is done. Find the value of  $n$  for this process. (The final equation can be solved by trial)

33. Air is expanded from a pressure of 200 to 25 psia with corresponding volume of  $43.2 \text{ ft}^3$  and temperature of 80 F while heat of amount 5 Btu is added. Find the value of  $n$  for this process, and the work transferred. (The final equation can be solved by trial)

34. Nitrogen is compressed in a polytropic process from  $p_1 = 10 \text{ psia}$  to  $p_2 = 100 \text{ psia}$  along a path for which  $n = 1.3$ . If the initial volume is  $10 \text{ ft}^3$  and initial temperature is 60 F, find the work and heat transferred and the change in entropy

35. Repeat Prob. 34, assuming that carbon dioxide is the fluid

36. Air is compressed along a polytropic path for which  $n = 1.2$ . The initial pressure is 20 psia, temperature is 80 F, and volume is  $5 \text{ ft}^3$ . The work added is 10 Btu. Compute the heat transferred and change in entropy, enthalpy, and internal energy

37. Repeat Prob. 36, assuming that hydrogen is the fluid

38. A mole of hydrogen expands in a polytropic process from  $p_1 = 25 \text{ psia}$  to  $p_2 = 50 \text{ psia}$  and  $t_2 = 800 \text{ F}$ . Find the heat and work transferred, change in entropy, and initial and final volumes if  $n = -3.0$

#### NONFLOW ISENTROPIC PROCESSES

39. One mole of nitrogen expands isentropically from  $p_1 = 100 \text{ psia}$  to  $p_2 = 10 \text{ psia}$ . If the initial temperature is 100 F, find the heat and work transferred and change in energy, enthalpy, and entropy

40. Repeat Prob. 39, assuming 1 lb<sub>m</sub> of air to be the fluid

41. A pound of air is isentropically compressed from  $-50 \text{ F}$  while the volume is halved. Find the work and heat transferred

42. A pound of argon is isentropically expanded from 300 F while the pressure is halved. Find the work transferred, change in internal energy, enthalpy, and entropy, and the expansion ratio

43. Air at 15 psia with volume of 10 ft<sup>3</sup> is isentropically compressed by transfer of 60 Btu of work until the temperature is 375 F. Find the mass of the air, change in enthalpy and energy, and the initial temperature.

44. A mole of oxygen at 20 psia and 100 F is isentropically compressed until the pressure is doubled. Determine the work transferred.

45. A mole of oxygen at 20 psia and 100 F is isentropically compressed until the volume is halved. Determine the work transferred.

46. One pound of air at a pressure of 100 psia and volume of 10 ft<sup>3</sup> is isentropically expanded until its volume is tripled. Determine the work transferred.

#### COMBINED NONFLOW PROCESSES

(Illustrate on  $pv$  and  $Ts$  diagrams)

47. A pound of air at a pressure of 25 psia and a temperature of 60 F is isentropically compressed until its enthalpy has increased by 50 Btu. It is then isothermally expanded to the original pressure and, finally, cooled at constant pressure to the original state. Find the work and heat transferred and the change in entropy for each process and for the cycle. Find the cycle efficiency.

48. A mole of air at 60 F is compressed along a polytropic path for which process  $n = 1.5$ , expanded isentropically to the initial temperature, and, finally, isothermally compressed back to the initial state with abstraction of 700 Btu of heat. Compute the heat and work transferred for each process and for the cycle.

49. A pound of nitrogen at 60 F is heated at constant volume until the pressure is doubled, expanded along a polytropic path ( $n = 1.2$ ) to the initial pressure, and, finally, cooled at constant pressure back to the initial state. Compute the heat, work, and change in entropy for each process and for the cycle.

50. Repeat Prob 49, assuming that the polytropic path is an isentropic path.

51. A pound of methane at 80 F is heated at constant pressure until the volume is doubled, compressed isothermally to the original entropy, expanded along a polytropic path ( $n = 1.2$ ) to the initial volume, and, finally, cooled to the initial state. Compute the heat and work transferred for each process and for the cycle.

52. Repeat Prob 49, assuming that the path of the polytropic process is unknown although the work of the cycle is 5 Btu.

#### COMBINED STEADY-FLOW PROCESSES

(Kinetic and potential effects neglected)

53. Repeat Prob 47, assuming that all processes are steady-flow processes. Compare answers to those for Prob 47.

54. Repeat Prob 53 for the data of Prob 48.

55. Repeat Prob 53 for the data of Prob 49.

56. Repeat Prob 53 for the data of Prob 50.

57. Repeat Prob 53 for the data of Prob 51.

#### STEADY-FLOW PROCESSES

(Kinetic energy of flow negligible unless otherwise stated)

58. A steady flow of air enters a system at a pressure of 15 psia and 60 F and leaves the system with pressure of 15 psia but temperature of 600 F. Find the heat and work transferred and change in entropy and enthalpy.

59. Repeat Prob 58, assuming that the specific volume remains constant and not the pressure

60. Nitrogen is isothermally compressed in a steady-flow system from 35 psia and 60 F to a state with entropy  $-0.2 \text{ Btu lb}_m^{-1} \text{ R}^{-1}$  less than the initial value. Determine the heat and work transferred if the mass flow rate is  $2 \text{ lb}_m \text{ sec}^{-1}$ .

61. A mole of air is compressed along a polytropic path with  $n = 1.30$  from  $p_1 = 20 \text{ psia}$  and  $t_1 = 60 \text{ F}$  to a state where the specific volume is  $150 \text{ ft}^3 \text{ mole}^{-1}$ . Find the work, heat, change in entropy, and enthalpy.

62. Repeat Prob 61, but assume  $n = 1.50$  and also  $n = 1.40$ .

63. Methane enters a system at low velocity and with pressure of 100 psia and temperature of 400 F and leaves the system at a pressure of 10 psia. (a) What is the maximum amount of kinetic energy that can be realized from this expansion if no heat is transferred? (b) Compute the maximum amount of work that can be obtained under the same conditions. (c) If the kinetic energy realized in (a) is dissipated within the flow system (throttling), what will be the temperature of the exit fluid (at pressure  $p_2 = 10 \text{ psia}$ )?

64. Helium enters a flow system with pressure of 10 psia and temperature of 100 F and leaves with a pressure of 100 psia. Determine the work required for isothermal and for isentropic compression.

65. Repeat Prob 64, assuming that the initial temperature is 0 F.

66. Air enters a compressor at  $p_1 = 14.7 \text{ psia}$  and  $t_1 = 60 \text{ F}$  and leaves at  $p_2 = 40 \text{ psia}$  and  $t_2 = 252 \text{ F}$ . Determine the work required if no heat is transferred. Can you prove that this process is irreversible?

67. For the data and pressure ratio of Prob 66 determine the work and heat transfers if  $t_1 = 60 \text{ F}$  and  $n = 1.45$ .

68. Repeat Prob 67, assuming that the process is adiabatic. Does this assumption mean that the process is irreversible?

#### MISCELLANEOUS INCLUDING AIR TABLE

69. Derive Eq (8-11)

70. Show by means of Boyle's and Joule's laws that for the Carnot cycle

$$\frac{-Q_R}{Q_A} = \frac{p_2 v_2}{p_1 v_1} = \frac{T_2}{T_1}$$

(Note Art 7-4)

71. A pound of air is heated at constant pressure from 60.3 to 1050.3 F. Determine the change in internal energy, enthalpy, and entropy and the values for heat and work transfers for this process.

72. Repeat Prob 71, assuming 1 mole of air and limits of 100.3 to 2990.3 F.

73. Air at 14.7 psia and 60.3 F is reversibly and adiabatically compressed to 147 psia. Determine the final temperature.

74. Air at 14.7 psia and 60.3 F is reversibly and adiabatically compressed to 700.3 F. Determine the final pressure.

75. Air at 14.7 psia and 60.3 F is irreversibly and adiabatically compressed to 147 psia and a temperature of 540.3 F. Compute the change in entropy.

76. Determine the work that can be done by an isentropic expansion of air from a pressure of 500 psia and 1000 F to 10 psia for both flow and nonflow processes.

77. Compressed air at 50 psia and 100 F is throttled through a globe valve to a pressure of 30 psia. The initial and final velocities of the air are negligible. For

this adiabatic process, determine the work and changes in entropy, enthalpy, and internal energy

### COMPRESSORS

78. Is Eq (8-22) valid for irreversible isothermal processes?

79. Derive an equation for the work of a compressor with clearance from the conventional indicator card if the compression is reversible and isothermal

80. For a nonflow compression process between definite pressure limits determine whether isothermal or isentropic compression will require the least work, or whether a decision can be made. What conclusions can be made for the inverse expansion process?

81. Show that if  $p_1 v_1^n = p_2 v_2^n$ , then  $p_1 V_1^n = p_2 V_2^n$

82. Determine the conventional work and horsepower for an air compressor with capacity of 500 cfm if the process is (a) isentropic, (b) polytropic with  $n = 1.3$  and (c) isothermal. Intake conditions are  $p = 14.7$  psia and  $t = 60$  F, and discharge pressure is 80 psia

83. For the data of Prob 82, determine the compressor displacement if  $c = 0.03$ , if  $c = 0.06$

84. Repeat Prob 82, assuming that methane is the gas

85. Air is reversibly compressed from  $p_1 = 14$  psia,  $t_1 = 80$  F, to  $p_2 = 60$  psia and  $t_2 = 295$  F, and the conventional volumetric efficiency is 94 per cent. Find the percentage of clearance

86. The compressor of Prob 82 is to be used at a location where the barometric pressure is 10 psia and  $t = 60$  F. What capacity is necessary if the same mass flow rate and the same discharge pressure are to be maintained? If the clearance is 0.06, what is the displacement of the compressor?

87. A double-acting 7- by 7-in air compressor, with clearance of 0.05, compresses air from  $p = 14.7$  psia and  $t = 70$  F to  $p = 100$  psia. Determine the (conventional) compressor capacity (300 rpm,  $n = 1.35$ )

88. How much cooling water ( $\text{lb}_m \text{ min}^{-1}$ ) must be supplied to the compressor of Prob 87 if the temperature rise of the water is 80 F?

89. For the data of Prob 87, determine the heat transferred to the cooling water during a compression and, also, during an expansion stroke (for air on one side of the piston only).

90. A double-acting air compressor delivers  $25 \text{ lb}_m \text{ min}^{-1}$  of air from  $p_1 = 14.7$  psia,  $t_1 = 80$  F, to  $p_2 = 100$  psia. Determine the shaft horsepower of the compressor if the isentropic compression efficiency is 82 per cent and the mechanical efficiency is 95 per cent (200 rpm,  $c = 0.05$ ,  $n = 1.3$ ). What is the value for the isothermal compression efficiency?

91. What will be the area of the indicator card for the data of Prob 87 if the spring scale is 100 psia in  $^{-1}$  and the reducing motion is 2 to 1? Draw a conventional  $pV$  card, and show true volumes

92. A two-stage double-acting compressor takes in air at  $p = 14.5$  psia,  $t_1 = 70$  F, and delivers it to a receiver at 300 psia. If the intercooling is perfect, determine the conventional horsepower, the capacity of the compressor, the heat transferred in the intercooler, the displacement and dimensions of both cylinders (150 rpm, 12- by 12-in low-pressure cylinder with 12-in stroke of high-pressure cylinder,  $c = 0.03$ ,  $n = 1.3$  for both cylinders)

93. Find the isothermal compression efficiency for the data of Prob 92

94. Determine the heat transferred to the coolant during a compression stroke of the first stage of Prob 92 (for air on one side of the piston only)

### Symbols

$a$	constant
$A$	constant, also, area
$b, B$	constants
$c$	heat capacity, also, compressor clearance
cfm	cubic feet per minute
$C$	constant, also, compressor capacity in cfm
$d$	diameter
$D$	compressor displacement in cfm
$e$	energy in general per unit mass
F	degrees Fahrenheit
FE	flow energy
$g_c$	dimensional constant
$h$	enthalpy per unit mass (thermal units)
ihp	indicated horsepower
imep	indicated mean effective pressure
$J$	Joule's equivalent
$k$	ratio of $c_p$ to $c_v$
KE	kinetic energy
$L$	stroke (length)
$M$	molecular weight
$m$	mass and mass flow rate
$n$	polytropic process
$N$	cycles per minute
$p$	pressure
PE	potential energy
$Q$	heat
$R$	universal or specific gas constant
R	degrees Rankine
rpm	revolutions per minute
$s$	entropy per unit mass (specific)
$t$	thermodynamic temperature
$T$	absolute thermodynamic temperature
$u$	internal energy per unit mass (thermal units)
$v$	volume per unit mass (specific)
$V$	volume
$W$	work
$\infty$	infinite

### Subscripts

$a$	atmospheric
conv	conventional
$c$	compression
$D$	displacement
$H$	high-pressure cylinder
$i$	intermediate (pressure)

<b>im</b>	indicated mean
<b>ind</b>	indicated
<b>irrev</b>	irreversible
<b>isen</b>	isentropic
<b>isoth</b>	isothermal
<b>L</b>	low-pressure cylinder
<b>m</b>	mechanical
<b>n</b>	polytropic process
<b>p</b>	constant pressure
<b>rev</b>	reversible
<b>ms</b>	multistage
<b>r</b>	relative
<b>v</b>	constant volume also, volumetric
<b>x</b>	process with constancy of process $x$

#### Greek Letters

$\eta_c$	(eta)	compression efficiency
$\eta_m$		mechanical efficiency
$\eta_v$		volumetric efficiency
$\Sigma$	(sigma)	summation

**CLASS ASSIGNMENTS**





## CHAPTER IX

### THE FLOW OF FLUIDS

The means for measuring fluid flows are important adjuncts to the thermodynamic study of the steady-flow process. The fluid flow may also have definite characteristics that must be ascertained before a thermodynamic analysis can be intelligently made. For certain machines, notably the turbine, creating a high velocity is the initial step in transforming available energy into work. All of these subjects are part of the problem of fluid flow.

In this chapter the units used will be restricted to the engineering system. In dealing with the perfect-gas laws the assumption of constancy of the heat capacities will be retained where simplicity is desirable.

**9-1. General Flow Equations for a Nozzle.** The time required for fluid to pass through a nozzle is extremely small, especially if the velocity is high. For this reason the expansion in a nozzle is essentially adiabatic. In Art. 3-6*d* the steady-flow equation was applied to reversible or irreversible processes and, for flow through the nozzle of real or perfect fluids,

$$Q - W = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2Jg_c}$$

Since  $Q$  and  $W$  are equal to zero,

$$\left. \frac{V_2^2 - V_1^2}{2Jg_c} \right]_{Q=0} = h_1 - h_2$$

and

$$V_2 \Big]_{Q=0} = \sqrt{2Jg_c(h_1 - h_2) + V_1^2} \quad (9-1)$$

This equation can also be written in the form<sup>1</sup>

$$V_2 \Big]_{Q=0} = F_c \sqrt{2Jg_c(h_1 - h_2)} \quad (3-16)$$

where the correction factor  $F_c$  equals

$$F_c = \sqrt{\frac{1}{1 - \left(\frac{A_2 v_1}{A_1 v_2}\right)^2}} \quad (3-17)$$

<sup>1</sup> The absolute value of  $\sqrt{2Jg_c}$  is 223.77

or

$$F_c = \sqrt{\frac{1}{1 - \beta^4 \left(\frac{v_1}{v_2}\right)^2}} \quad (9-2)$$

where

$$\beta = \frac{D_2}{D_1} = \frac{\text{diameter of smallest section of the nozzle}}{\text{diameter of approach section of the nozzle}}$$

The ideal maximum velocity will be attained when the expansion is reversible, and therefore, since the process is also adiabatic, the entropy remains constant

$$V_{2 \text{ rev}} = F_c \sqrt{2Jg_c(h_1 - h_2)_{s=c}} \quad (9-3)$$

If these equations are restricted to fluids that obey, at least approximately, the laws that govern perfect gases, Eq (3-16) can be expanded (refer to Art 8-8)

$$V_{2 \text{ rev or irrev}} = F_c \sqrt{2Jg_c c_p (T_1 - T_2)} = F_c \sqrt{2Jg_c c_p T_1 \left(1 - \frac{T_2}{T_1}\right)} \quad (9-4a)$$

$$= F_c \sqrt{2Jg_c c_p T_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right]} = F_c \sqrt{\frac{2g_c k R T_1}{(k-1)} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right]} \quad (9-4b)$$

When Eq (9-3) is treated in similar manner,

$$V_{2 \text{ rev}} = F_c \sqrt{2Jg_c c_p T_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]_{s=c}} \quad (9-5a)$$

$$= F_c \sqrt{\frac{2g_c k R T_1}{(k-1)} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]_{s=c}} \quad (9-5b)$$

Equations involving  $k$  are preferable to those involving  $c_p$  since  $k$  varies somewhat less with temperature than  $c_p$  (Fig I, Appendix)

The mass flow rate is determined directly from the continuity equation

$$m = \frac{A V}{v} \quad (3-14)$$

The usual engineering units for these equations are

$V$  = velocity (ft/sec)

$h$  = enthalpy (Btu/lb<sub>m</sub>)

$c_p$  = heat capacity (Btu/lb<sub>m</sub> R)

$T$  = absolute thermodynamic temperature (R)

$R$  = specific gas constant  $\left(\frac{1,545 \text{ ft lb}_f}{M \text{ lb}_m \text{ R}}\right)$  or  $\left(\frac{1,986 \text{ Btu}}{M \text{ lb}_m \text{ R}}\right)$

$J$  = Joule's equivalent (778 16 ft lb<sub>f</sub>/Btu)

$M$  = molecular weight

$$g_c = 32.17 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}$$

**9-2. General Design of the Nozzle.** The shape of a nozzle that will at least theoretically allow the attainment of the ideal velocity will be illustrated by an example. Here, for generality, a real and not a perfect fluid will be used, while for simplicity the flow will be from a region of zero velocity in order that the correction factor will be 1.0

**Example 1.** Determine the variation in area throughout a nozzle that is to expand steam isentropically from  $p_1 = 100$  psia and  $t_1 = 600$  F to  $p_2 = 20$  psia if the initial velocity is zero

**Solution:** The simplest solution is to use Steam Table 3

$$\begin{aligned} v_1 &= 6\,218 \text{ ft}^3/\text{lb}_m & \text{Keenan and Keyes} \\ h_1 &= 1329.1 \text{ Btu}/\text{lb}_m & \text{Steam Tables} \\ s_1 &= 1.7581 \text{ Btu}/\text{lb}_m \text{ F} \end{aligned}$$

Selection of pressure at any stage of the expansion can be arbitrary, while entropy must be held constant at  $s = 1.7581$ . Interpolation of Steam Table 3 for pressures of 100, 80, 60, 54.6, 40, and 20 psia yields the results indicated in the accompanying table

$p$ psia	$h$ Btu lb <sub>m</sub> <sup>-1</sup>	$v$ ft <sup>3</sup> lb <sub>m</sub> <sup>-1</sup>
100	1329.1	6.218
80	1304.1	7.384
60	1273.8	9.208
54.6	1265.0	9.844
40	1234.2	12.554
20	1174.8	21.279

With these values the velocity can be found from Eq. (9-3) and the area from Eq. (3-14) and for unit mass flow rate

$p$ psia	$V$ ft sec <sup>-1</sup>	$A$ ft <sup>2</sup>
100	0	∞
80	1,119	0.0066
60	1,660	0.00556
54.6	1,790	0.00550
40	2,175	0.00577
20	2,775	0.00768

The velocities, specific volumes, and areas found in Example 1 are plotted in Fig 9-1 against the corresponding pressures. Study of Fig 9-1 reveals an odd result. The area of the nozzle decreases as the pressure decreases until a minimum area, called the *throat*, is reached; from here on the area increases. The explanation, however, is indicated by Fig 9-1 and the continuity equation. In the early stages of the expansion the velocity increases at a greater rate than the specific volume, this causes a reduction of area for constant mass flow

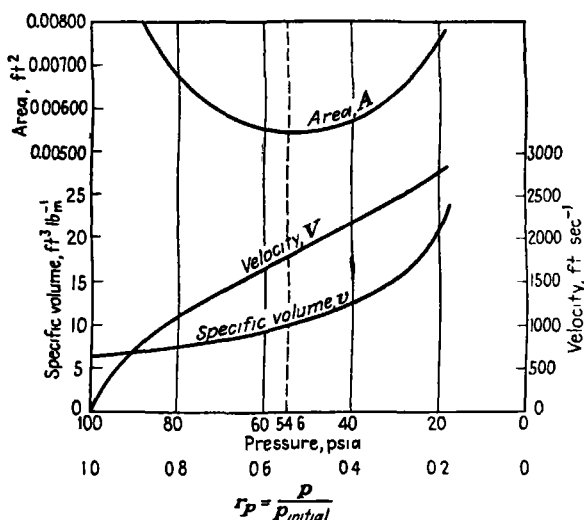


FIG 9-1 Relations of area, velocity, and specific-volume in a convergent-divergent nozzle

After the throat, the velocity increases at a lesser rate than the specific volume, and, therefore the area must increase for this part of the expansion. If the expansion does not proceed over a wide pressure range, only the convergent section may be necessary. In Example 1 this would be true for expansions from 100 psia down to the throat value of approximately 55 psia. A nozzle of this type is called a *convergent nozzle*. However, if the pressure at exit of the nozzle is less than 55 psia (for the data of Example 1), a divergent section must also be used to attain the maximum velocity. Nozzles of this type are called *convergent-divergent nozzles*.

The calculations in Example 1 determined the area of the nozzle at several different states of the expansion. At each state there will be a definite pressure and a definite velocity. Since the length of the nozzle does not enter the calculations for either pressure or velocity,

then the nozzle can have any length. If the nozzle is very short, the transition from the high- to the low-pressure region is quickly accomplished. If the nozzle is made longer, the transition will occur over a proportionately longer period of time, although obviously the same sequence of areas is visited in either case. The nozzle is constructed in the manner illustrated in Fig 9-2. At the start of the expansion the velocity is zero, and therefore the area should be infinite. To approach this condition the walls of the nozzle can be made tangent to the walls of the reservoir, as illustrated in Fig 9-2, although, practically, the shape of the nozzle at this location is not critical since the

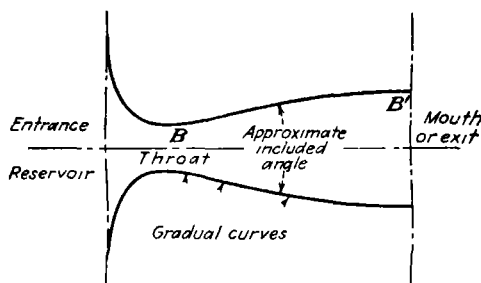


FIG 9-2 Convergent-divergent nozzle

velocity is low. The converging section of the nozzle need follow no particular type of curve, and any shape is acceptable that allows the area to decrease continually. From experience it is found that the convergent part can be made quite short in length with no ill effects, and this is done to reduce friction. For the same reason the walls of the nozzle should be well polished. However, the divergent part of the nozzle must be more carefully treated because here the velocities are quite high. The throat of the nozzle should merge into the divergent section, as shown at *B* in Fig 9-2, without a corner or discontinuity in the curve that would cause an abrupt change in direction of the fluid and a disturbance to be set up in the high-velocity stream. Similarly, the diverging walls must continue to curve gradually and become parallel at exit (*B'*) if the fluid is to leave the nozzle without disturbances created by an abrupt change in direction, for here the velocity of the fluid is extremely high. While the diverging section should be short if friction losses are to be avoided, still, the divergence cannot be too great or the fluid will break away from the walls and complete the expansion in a turbulent manner outside the nozzle. If the included angle (approximately measured) of the nozzle is small, the less critical will be the design, and any smooth curve between throat and exit will

yield good results. For this reason, the included angle of most nozzles is less than 20 deg, and smaller values of the order of 6 to 12 deg may be preferable

Note that the basic dimensions for a nozzle are the mouth and throat areas. With these dimensions a nozzle can be constructed in the fashion of Fig 9-2. Since the pressure at the exit is known, the area and velocity at this section can be directly computed. However, the throat area cannot be computed unless the pressure at this section is known. This could be found as in Example 1 by plotting the entire area demands of the nozzle although an easier method will be found in the next section.

**9-3. The Throat Pressure Ratio.** To discover the factors that necessitate a convergent-divergent nozzle, the perfect-gas laws allow the simplest presentation. Consider a perfect gas expanding from a region of high pressure. Inspection of the continuity equation and of Fig 9-1 for a real fluid shows that for a given flow rate the ratio of  $V/v = m/A$  determines the area variation for the nozzle. If the ratio of velocity to specific volume continually increases, only a convergent nozzle is necessary, and the exit area is the throat area. If the ratio passes through some maximum value and then decreases, a convergent-divergent nozzle is necessary, and the minimum or throat area is not at the exit of the nozzle. The pressure ratio where  $V/v$  becomes a maximum is found by setting the derivative of  $V/v$  with respect to pressure ratio equal to zero:

$$\frac{d(V_2/v_2)}{d(p_2/p_1)} = 0$$

Equation (9-4b) is divided by  $v_2$  where  $v_2$  is determined by

$$p_2 v_2^n = p_1 v_1^n \quad \text{or} \quad v_2 = v_1 \left( \frac{p_1}{p_2} \right)^{\frac{1}{n}} \quad \text{and} \quad \frac{1}{v_2} = \frac{1}{v_1} \left( \frac{p_2}{p_1} \right)^{\frac{1}{n}}$$

The correction factor, for the velocity of approach, and  $r_p$ , the ratio of  $p_2/p_1$ , are inserted

$$\frac{V_2}{v_2} = \sqrt{\frac{2g_c k R T_1}{(k-1)v_1^2} \left[ \frac{r_p^{\frac{2}{n}} - r_p^{\frac{n+1}{n}}}{1 - \beta^4 r_p^{\frac{2}{n}}} \right]} \quad (9-6)$$

Equation (9-6) is differentiated with  $k$  and  $n$  treated as constants and therefore  $r_p$  is the only variable

$$\frac{d(v_2/v_1)}{d(r_p)} = (1 - \beta^4 r_p^{\frac{2}{n}}) \left( \frac{2}{n} r_p^{\frac{2}{n}-1} - \frac{n+1}{n} r_p^{\frac{1}{n}} \right) - (r_p^{\frac{2}{n}} - r_p^{\frac{n+1}{n}}) \left( -\frac{2}{n} \beta^4 r_p^{\frac{2}{n}-1} \right) = 0$$

which reduces to

$$r_{pt}^{\frac{1-n}{n}} + \frac{n-1}{2} \beta^4 r_{pt}^{\frac{2}{n}} = \frac{n+1}{2} \quad (9-7)$$

where  $r_{pt}$  is the pressure ratio between entrance and throat

When this equation is solved for various values of  $\beta$  and  $n$ , results are as indicated in Table 9-1

TABLE 9-1 —VALUES OF  $r_{pt}$  FOR VARIOUS  $n$  VALUES\*

$\beta$	$n = 1.25$	$n = 1.30$	$n = 1.35$	$n = 1.40$	$n = 1.45$
0	0.555	0.546	0.537	0.528	0.520
0.20	0.555	0.546	0.537	0.529	0.521
0.40	0.558	0.549	0.540	0.532	0.524
0.60	0.572	0.563	0.554	0.546	0.538
0.80	0.617	0.609	0.601	0.593	0.545

\* Abstracted from reference 1

When the velocity of approach is zero, Eq (9-7) equals

$$r_{pt} = \frac{p_t}{p_1} = \left( \frac{2}{n+1} \right)^{\frac{n}{n-1}} \quad (9-8)$$

The *minimum throat pressure ratio*  $r_{pt}$  is more often called the *critical pressure ratio* although the term is somewhat misleading because the word *critical* is associated with other fluid properties (Arts 6-2 and 7-11)

Although the derivation was for perfect gases, the relationships developed will hold within experimental accuracy for real fluids if the adiabatic  $pv$  path can be represented by the equation

$$pv^n = C$$

This statement can be checked by the data of Example 1. For these data the exponent  $k$  is more appropriate than the general exponent  $n$ , because  $k$  is invariably used as a symbol to designate the isentropic expansion

$$\left( \frac{p_2}{p_1} \right) = \left( \frac{v_1}{v_2} \right)^k$$



Solving for  $k$  (although values for  $k$  are given in Fig 8 of the Keenan and Keyes Steam Tables) gives the results indicated in the accompanying table.

$p$	$v$	$p_2/p_1$	$k$
100	6 218	0 8	1 30
80	7 384	0 75	1 30
60	9 208	0 666	1 30
40	12 554	0 5	1 31
20	21 279		

If 1.30 is selected as a probable value,

$$r_{pt} = \left(\frac{p_t}{p_1}\right) = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} = \left(\frac{2}{2.3}\right)^{4.34} = 0.546$$

and

$$p_t = 100(0.546) = 54.6 \text{ psia}$$

Inspection of Fig 9-1 confirms this answer, as the minimum area occurs at this pressure

For superheated steam the isentropic process can be closely followed by the polytropic equation

$$pv^k = C \quad k \approx 1.30 \quad (9-9a)$$

For wet steam an average value assigned to  $k$  is

$$k \approx 1.13 \quad (9-9b)$$

With these values (or better, more precise values calculated as in the foregoing table)

$$r_{pt} = 0.545 \quad \text{superheated steam} \quad (9-10a)$$

$$r_{pt} = 0.58 \quad \text{wet steam} \quad (9-10b)$$

**Example 2.** Find the necessary dimensions for a perfect nozzle that will allow a mass flow of  $1.0 \text{ lb}_m \text{ sec}^{-1}$  of air from a large system at 50 psia and 60 F to a discharge region of 10 psia.

**Solution.** Since the pressure range is large, it is suspected that the throat of the nozzle will have a higher pressure than the exit pressure. Testing this surmise by Eq (9-8) with  $n = k = 1.4$  or by Table 9-1 gives

$$r_{pt} = \frac{p_t}{p_1} = \left(\frac{2}{n+1}\right)^{\frac{n}{n-1}} = \left(\frac{2}{2.4}\right)^{1.4} = 0.528$$

$$p_t = 50(0.528) = 26.4 \text{ psia}$$

The velocity at the throat is determined from Eq (9-5a)

$$V_{t \text{ rev}} = \sqrt{2Jg_c c_p T_1 \left[ 1 - (0.528)^{\frac{k-1}{k}} \right]} \quad (9-5a)$$

Selecting  $c_p$  from Fig 1A (Appendix) and noting that 223.77 is the numerical value of  $\sqrt{2g_c J}$ , will give

$$\begin{aligned} V_{t \text{ rev}} &= 223.77 \sqrt{0.24(520)[1 - (0.528)^{0.286}]} \\ V_{t \text{ rev}} &= 1,017 \text{ ft/sec} \end{aligned}$$

The initial specific volume can be found by the equation of state

$$\begin{aligned} v_1 &= \frac{RT_1}{p_1} = \frac{1545(520)}{29(50)(144)} \\ &= 3.86 \text{ ft}^3/\text{lb}_m \end{aligned}$$

The specific volume at the throat is equal to

$$\begin{aligned} v_t &= v_1 \left( \frac{p_1}{p_t} \right)^{\frac{1}{k}} \\ &= 3.86(1.893)^{0.715} \\ &= 6.09 \text{ ft}^3/\text{lb}_m \end{aligned}$$

By the continuity equation

$$\begin{aligned} m &= \frac{AV}{v} \\ A_t &= \frac{1.0(6.09)}{1017} = 0.00598 \text{ ft}^2 \quad \text{Ans.} \end{aligned}$$

The velocity at the mouth of the nozzle equals

$$\begin{aligned} V_{2 \text{ rev}} &= \sqrt{2Jg_c c_p T_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \\ &= 223.77 \sqrt{0.24(520)[1 - (0.2)^{0.286}]} \\ &= 1,515 \text{ ft/sec} \end{aligned}$$

The specific volume at the mouth equals

$$\begin{aligned} v_2 &= v_1 \left( \frac{p_1}{p_2} \right)^{\frac{1}{k}} \\ &= 3.86(5)^{0.715} \\ &= 12.2 \text{ ft}^3/\text{lb}_m \end{aligned}$$

and the area is equal to

$$A_2 = \frac{mv}{V} = \frac{1.0(12.2)}{1,515} = 0.00805 \text{ ft}^2 \quad \text{Ans}$$

**Example 3.** Repeat Example 2 for the same conditions except that  $\beta = 0.70$  (entrance to throat)

**Solution:** From Table 9-1 (interpolating)

$$r_{pt} = 0.569$$

Hence,

$$p_t = 50(0.569) = 28.5 \text{ psia}$$

The velocity at the throat equals

$$\begin{aligned} V_{t \text{ rev}} &= \sqrt{\frac{2Jg_c c_p T_1 \left[ 1 - (r_{pt})^{\frac{k-1}{k}} \right]}{[1 - \beta^4(v_1/v_2)^2]}} \\ &= 223.77 \sqrt{\frac{0.24(520)[1 - (0.569)^{0.286}]}{[1 - 0.80^4(0.668)^2]}} \\ &= 1,030 \text{ ft/sec} \end{aligned}$$

and

$$\begin{aligned} v_1 = \frac{RT_1}{p_1} &= \frac{1,545(520)}{29(50)144} = 3.86 \text{ ft}^3/\text{lb}_m & v_t &= \left(\frac{p_1}{p_t}\right)^{\frac{1}{k}} v_1 \\ & & &= (1.76)^{0.715} (3.86) \\ & & &= 5.79 \text{ ft}^3/\text{lb}_m \end{aligned}$$

The area at the throat equals

$$A_t = \frac{mv}{V} = \frac{1.0(5.79)}{1,030} = 0.00561 \text{ ft}^2 \quad \text{Ans}$$

The velocity at exit can be found in the same manner by Eq. (9-1) with subscript 2 identifying the exit section and subscript 1 identifying the throat section

**9-4. Velocity and Pressure Variations in the Nozzle.** Consider a convergent nozzle leading from a region of high pressure to a receiver that can be maintained at any desired exhaust pressure. When the pressure in the receiver is equal to the initial pressure, flow cannot occur. But when the pressure in the receiver is lowered, the pressure at the throat is lowered to the same value and flow begins. Inspection of Eq. (9-4b) shows that the velocity increases as the exhaust pressure decreases. However, when the receiver pressure has been reduced to the pressure dictated by the critical pressure ratio, a maximum velocity will be attained that cannot be exceeded (at the throat) by again lowering the exhaust pressure. The convergent nozzle can only expand fluid to the critical pressure ratio because for any additional expansion a divergent section is required by the nozzle, this is evident from Art. 9-3. For this reason, the pressure at the throat of a convergent nozzle is also the receiver pressure if this pressure is equal to or higher than that defined by the critical ratio. If the receiver pressure is reduced below the critical value, the pressure at the exit from the nozzle—and this is the throat—will be that of the critical ratio. The fluid will expand to this pressure, but, since the divergent section is missing, further expansion will not occur in the nozzle. Instead, the fluid leaving the nozzle will suffer a wild, turbulent expansion to the exhaust pressure with acquisition of little or no additional velocity.

Suppose that a convergent nozzle is compared with a convergent-divergent nozzle under conditions such that the pressure ratio between source and receiver is less than the critical ratio. Both nozzles would have the same values for pressure (and velocity) at the throat, but in the convergent-divergent nozzle higher velocities will be found after the throat because the diverging section is present to guide and control the expansion.

Thus, it appears that the velocity of the fluid at the throat of either a convergent or a convergent-divergent nozzle is restricted to some limiting value by the critical pressure ratio. It will be of interest to investigate the limiting value that can be attained by the throat velocity, and, to do this, the perfect-gas laws allow the simplest derivation. For conditions of zero velocity of approach the maximum velocity at the throat of a nozzle can be found by substituting Eq. (9-8)

$$r_{pt} = \frac{p_t}{p_1} = \left( \frac{2}{k+1} \right)^{\frac{k}{k-1}} \quad (\text{for } n = k) \quad (9-8)$$

and, by substituting Eq. (7-11),

$$c_p = \frac{kR}{k-1}$$

into the isentropic Eq. (9-5a)

$$V_{t \text{ rev}} = \sqrt{2Jg_c c_p T_1 \left[ 1 - \left( \frac{p_t}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (9-5a)$$

This simplifies to

$$V_{t \text{ rev}} = \sqrt{2g_c \frac{kRT_1}{k-1}} \quad (a)$$

The temperature at the throat is

$$T_t = T_1 \left( \frac{p_t}{p_1} \right)^{\frac{k-1}{k}} = T_1 \left( \frac{2}{k+1} \right)$$

and this value, substituted in Eq. (a), gives

$$V_{t \text{ rev}} = \sqrt{g_c k R T_t} = \sqrt{g_c k p_t v_t} \quad (9-11)$$

Inspection of Eq. (9-11) shows that the velocity at the throat of an ideal nozzle is dependent only upon temperature. But this same conclusion was obtained from the equation derived in Prob. 24, Chap. I, for the velocity of propagation of sound (the acoustic velocity) or of small pressure disturbances in a compressible medium. In fact, when

the constant for this latter equation is evaluated by experimental tests, it is found to be equal to  $gk$ . Thus, the maximum velocity that can be attained in the convergent part of a nozzle is the acoustic velocity.

However, when the pressure ratio between entrance and exit of the convergent-divergent nozzle is less than the critical pressure ratio, the velocity of the fluid in the divergent section will be far greater than the throat velocity. Mach numbers greater than one, that is, velocities greater than the acoustic velocity, can be achieved in the divergent section of the nozzle. The Mach number is defined

$$Ma = \frac{V}{V_a} \quad (9-12)$$

and is the ratio of the actual velocity to the acoustic velocity computed for the state where the velocity  $V$  exists.

When the pressure ratio between entrance and throat of the nozzle is greater than the critical ratio, then the pressure ratio between the entrance and the diverging section must also be greater than the throat ratio. For only when the critical ratio exists at the throat can the pressures in the diverging section fall below the critical value. In this case the divergent section is a diffuser slowing down the velocities and achieving higher pressures (Art 4-3). The possible conditions that can exist in the convergent-divergent nozzle are illustrated in Fig 9-3. In curve  $A$  (and probably curve  $B$ ) the nozzle acts as a venturi, a pressure at the exit slightly lower than that at the entrance causes a greatly decreased pressure at the throat. In the convergent section, expansion proceeds with the attainment of a high velocity and a low pressure at the throat. In the divergent section, compression occurs, the velocity being progressively reduced while the pressure is increased. This venturi action continues as long as the throat pressure is greater than, or equal to, the critical value.

When the pressure at the exit of the nozzle is less than the throat pressure and the exit area has been proportioned in accordance with the correct values for pressure and velocity, the expansion line for the nozzle will be a smooth curve such as  $E$  (Fig 9-3). Here the critical pressure ratio occurs at the throat, but lower pressures and higher velocities occur in the divergent section.

If the pressure at the exit is gradually raised, the fluid will persist in expanding almost to the former exit pressure, probably because of the adherence of the fluid to the walls. However, at some stage, a *compression shock* will occur when the supersonic-velocity fluid strikes the higher density fluid at or near the exit. When compression shock

occurs, the velocity becomes subsonic and the fluid is irreversibly compressed. The pressure increases but never to a degree that could be attained by an isentropic compression, and, because of this irreversibility, the pressure after the shock may be lower than the pressure at the throat (curve *D*). Note that by the continuity equation the velocity can vary widely at any area because of the compensating effect of the specific volume. After the shock the diverging section of

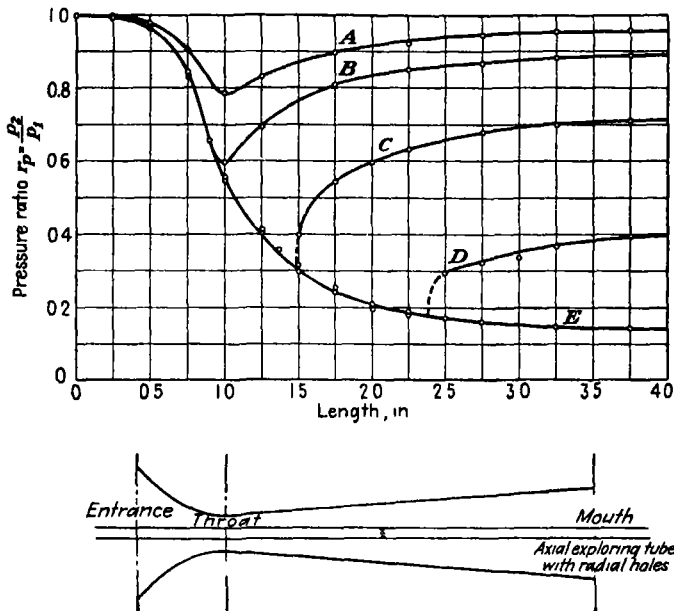


FIG 9-3 Variations of pressure conditions in a convergent-divergent nozzle

the nozzle acts as a diffuser, and the subsonic velocity is reduced to a still lower value, while the pressure is increased to the discharge pressure

Thus, the convergent-divergent nozzle may act either as a nozzle or as a venturi, and because of this, the throat pressure cannot readily be predicted. For the convergent nozzle either the pressure at the throat is that dictated by the critical ratio, or else it is the exhaust pressure. For the convergent-divergent nozzle the pressure at the throat is either the pressure dictated by the critical ratio or else a higher pressure that is less than the exhaust pressure.

**9-5. Efficiency and Velocity Coefficients.** The *efficiency* of the nozzle is defined as the ratio of the actual kinetic energy to the maximum value that could be realized by an isentropic expansion from the

initial state to the final state This ideal kinetic energy can be found from the steady-flow equation restricted to an isentropic process

$$h_1 + \frac{V_1^2}{2Jg_c} = h_2 + \frac{V_{isen}^2}{2Jg_c} \quad (Q = W = 0)$$

$$\frac{V_{isen}^2}{2Jg_c} = \frac{V_1^2}{2Jg_c} + (h_1 - h_2)_{s-c}$$

And by definition

$$\eta_n = \frac{\text{actual KE}}{\text{ideal KE}} = \frac{V_2^2}{V_{isen}^2} = \frac{V_2^2/2Jg_c}{V_1^2/2Jg_c + (h_1 - h_2)_{s-c}} \quad (9-13)$$

The *velocity coefficient* is defined as the ratio of the actual velocity to the ideal velocity

$$C_v = \frac{\text{actual velocity}}{\text{ideal velocity}} = \frac{V_2}{V_{isen}} = \sqrt{\eta_n} \quad (9-14)$$

The nozzle is a remarkably efficient device, with the efficiency varying in general with the length and roughness of the inner surface For convergent nozzles, efficiencies of 98 per cent and velocity coefficients of 99 per cent are quite usual values Convergent-divergent nozzles must be quite long as compared with convergent nozzles if the cone angle of the divergent section is to be held to small values The velocity in the divergent section is high, being greater than the acoustic velocity, and friction loss is increased For this reason, the over-all efficiency of a convergent-divergent nozzle is usually lower than that for a convergent nozzle, although values above 90 per cent are quite usual If venturi action occurs and the velocity at the throat is not high, the compression process in the divergent section can be accomplished without seriously interfering with the efficiency values given above for convergent nozzles However, if the throat velocity approaches the acoustic value, the compression is not readily performed without turbulence that causes lower efficiencies

**Example 4:** Determine the dimensions for a nozzle that is to expand  $1 \text{ lb}_m \text{ sec}^{-1}$  of steam from  $p_1 = 100 \text{ psia}$  and  $t_1 = 600 \text{ F}$  to  $p_2 = 20 \text{ psia}$  if the velocity coefficient from entrance to throat is assumed to be 0.99, and from entrance to exit 0.96 (Velocity of approach is negligible, data are basically the same as in Example 1)

**Solution:** The same method of solution should be used as in Example 1 Assume a pressure and find the velocity and specific volume at that pressure With this information, the area corresponding to each pressure can be found Suppose the first pressure selected is  $54.6 \text{ psia}$ , which was the throat pressure in Example 1

$$p_2 = 54.6 \text{ psia}$$

$$h_1 = 1329.1 \text{ Btu/lb}_m$$

$$h_2 = 1265.0 \text{ Btu/lb}_m$$

$$V_{2 \text{ rev}} = 1,790 \text{ ft/sec}$$

With these data

$$V_{2'} = C_v V_{2 \text{ isen}} = 0.99(1,790) = 1,773 \text{ ft/sec}$$

But the actual velocity also equals

$$V_{2'} = \sqrt{2Jg_c(h_1 - h_{2'})} = C_v \sqrt{2Jg_c(h_1 - h_{2'})_{\text{isen}}} = \sqrt{2Jg_c\eta_n(h_1 - h_{2'})_{\text{isen}}}$$

Therefore,

$$\begin{aligned} h_1 - h_{2'} &= C_v^2(h_1 - h_{2'})_{\text{isen}} = \eta_n(h_1 - h_{2'})_{\text{isen}} \\ &= (0.99)^2(64.1) \\ &= 62.8 \text{ Btu/lb}_m \end{aligned}$$

or

$$\begin{aligned} h_{2'} &= h_1 - 62.8 = 1329.1 - 62.8 \\ &= 1,266.3 \text{ Btu/lb}_m \end{aligned}$$

Since enthalpy and pressure are known to be

$$p_2 = 54.6 \text{ psia} \quad h_{2'} = 1,266.3 \text{ Btu/lb}_m$$

the Steam Tables yield

$$v_{2'} = 9.946 \text{ ft}^3/\text{lb}_m$$

With these values the area is found from the continuity equation

$$\begin{aligned} A_{2'} &= \frac{mv}{V} = \frac{1.0(9.946)}{1,773} \\ &= 0.0056 \text{ ft}^2 \quad \text{Ans} \end{aligned}$$

However, this area is not necessarily the throat area since the derivation of Art. 9-3 showed that the throat pressure is governed by the  $n$  value of the expansion, and here the  $n$  value is not the isentropic value. But it is not unusual to assume that the answer found above is the corrected throat area if only because the equations in this chapter rest upon the assumption that the velocity distribution is uniform at any section of the nozzle (and, too, the amount of irreversibility is small). Actually, some nonuniformity must be present, and this nonuniformity of velocity will be increased by friction since friction will probably be initiated at the walls. These elementary equations, then, are not precisely true, and therefore it can be assumed, for simplicity, that the answer given above is the throat area. With this reasoning, it is not necessary to chart out the complete area-pressure relationships since a higher degree of precision is not warranted.

In the same manner the conditions at the mouth of the nozzle are found, although here the pressure is fixed by the receiver. From Example 1

$$\begin{aligned} h_1 &= 1329.1 \text{ Btu/lb}_m \\ \Delta h_{\text{isen}} &= -154.3 \text{ Btu/lb}_m \\ V_{3 \text{ isen}} &= 2,775 \text{ ft/sec} \end{aligned}$$

With these data

$$V_{3'} = C_v V_{3 \text{ isen}} = 0.96(2,775) = 2,664 \text{ ft/sec}$$

The enthalpy is

$$\begin{aligned} h_{3'} &= h_1 + C_v^2(\Delta h_{\text{isen}}) \\ &= 1329.1 - (0.96)^2(154.3) \\ &= 1186.8 \text{ Btu/lb}_m \end{aligned}$$



The specific volume corresponding to

$$p_1 = 20 \text{ psia} \quad h_{1'} = 1186.8 \text{ Btu/lb}_m$$

is found from the Steam Tables to be

$$v_{1'} = 22.05 \text{ ft}^3/\text{lb}_m$$

It is again noted that the effect of friction is to dissipate kinetic energy, hence, the velocity decreases and the enthalpy and specific volume increase. From the continuity equation

$$\begin{aligned} A_{2'} &= \frac{mv}{V} = \frac{1.0(22.05)}{2.664} \\ &= 0.00828 \text{ ft}^2 \quad \text{Ans} \end{aligned}$$

**Example 5:** Determine the dimensions for a nozzle that is to expand  $1 \text{ lb}_m \text{ sec}^{-1}$  of air from a large system at 50 psia and 60 F to a discharge region at 10 psia. Nozzle efficiency at the throat is assumed to be 0.98, and at the mouth 0.92. (Velocity of approach is negligible, data are basically the same as in Example 2.)

**Solution:** (The comments in Example 4 apply, as well, to this solution.) The data from Example 2 are

$$\begin{aligned} p_2 &= 26.4 \text{ psia} \\ V_{2 \text{ rev}} &= 1.017 \text{ ft/sec} \end{aligned}$$

Here the coefficient of velocity is 0.99 and

$$V_{2'} = 0.99(1.017) = 1.007 \text{ ft/sec}$$

The dissipation of kinetic energy equals

$$\Delta h_{\text{reheat}} = \frac{V_2^2 - V_{2'}^2}{2Jg_c} = \frac{(1.017)^2 - (1.007)^2}{64.4(778.16)} = 0.42 \text{ Btu/lb}_m$$

Hence, the enthalpy is increased by this amount while the temperature increase is

$$\begin{aligned} c_p \Delta t_{\text{reheat}} &= \Delta h_{\text{reheat}} \\ \Delta t_{\text{reheat}} &= \frac{0.42}{0.24} \approx 2 \text{ F} \end{aligned}$$

The ideal temperature at the given pressure is

$$\begin{aligned} \frac{T_2}{T_1} &= \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} = (0.528)^{0.286} \\ T_1 &= 433 \text{ R} \end{aligned}$$

Hence,

$$T_{2'} = 433 + 2 = 435 \text{ R}$$

The specific volume equals

$$\begin{aligned} v_2 &= \frac{RT}{p} = \frac{1545(435)}{26.4(144)} \\ &= 6.10 \text{ ft}^3/\text{lb}_m \end{aligned}$$

and by the continuity equation

$$A_{2'} = \frac{mv}{V} = \frac{1.0(6.10)}{1,007}$$

$$A_{2'} = 0.00605 \text{ ft}^2 \quad \text{Ans}$$

Here, for the same reasons as in Example 4, the answer, with adequate precision, can be assumed to be the throat area

At the mouth of the nozzle

$$V_{3'} = 1,515(0.92)^{\frac{1}{2}}$$

$$= 1,453 \text{ ft/sec}$$

The ideal temperature at the mouth is

$$\frac{T_3}{T_1} = \left(\frac{p_3}{p_1}\right)^{\frac{k-1}{k}} = \left(\frac{10}{50}\right)^{0.286}$$

$$T_3 = 328 \text{ R}$$

The reheat because of friction is

$$\frac{V_3^2 - V_{3'}^2}{2Jg_c} = \frac{1,515^2 - 1,453^2}{64.4(778)} = 3.8 \text{ Btu/lb}_m$$

$$\Delta t_{\text{reheat}} = \frac{3.8}{0.24} \approx 16 \text{ F}$$

Hence,

$$T_{3'} = 344 \text{ R}$$

The specific volume is

$$v_3 = \frac{RT}{p} = \frac{1.44 \frac{\text{ft}^2}{\text{lb}_m} (344)}{10(144)} = 12.72 \text{ ft}^3/\text{lb}_m$$

The area at the mouth is

$$A_{3'} = \frac{mv}{V} = \frac{1.0(12.72)}{1,453} = 0.00875 \text{ ft}^2 \quad \text{Ans}$$

**9-6. Expanded Velocity Equations.** When Eq (9-5) is used for small pressure ratios, the difference term will approach zero. Any slight variation in calculating this difference will lead to relatively large errors in the computed velocity. To remedy this difficulty the term can be expanded<sup>1</sup> into a power series that is rapidly convergent. By this means Eq (9-5) can be written for the ideal velocity

$$V_{2 \text{ rev}} = \sqrt{\frac{2g_c R T_1 \left[ \frac{p_1 - p_2}{p_1} + \frac{1}{2k} \left( \frac{p_1 - p_2}{p_1} \right)^2 + \dots \right]}{[1 - \beta^4 (v_1/v_2)^2]}} \quad (9-15a)$$

<sup>1</sup> MacLaurin's series

$$f(x) = f(0) + f'(0)x + \frac{f''(0)}{2!} x^2 + \dots$$

Rewrite  $\frac{p_2}{p_1}$  in form

and, for small pressure drops,

$$V_{2 \text{ rev}} = \sqrt{\frac{2g_c R T_1 \left[ \frac{p_1 - p_2}{p_1} \right]}{[1 - \beta^4]}} \quad (9-16a)$$

Equation (9-16a) can be rewritten by substituting

$$\frac{R T_1}{p_1} = v_1$$

to give

$$V_{2 \text{ rev}} = \sqrt{\frac{2g_c v_1 (p_1 - p_2)}{1 - \beta^4}} \quad (9-17)$$

The pressure difference ( $p_1 - p_2$ ) could be balanced by a column of the flowing fluid  $H$  ft in height and of constant density  $\rho_1$

$$p_1 - p_2 = \rho_1 H \frac{g}{g_c}$$

and

$$v_1 (p_1 - p_2) = H \frac{g}{g_c}$$

When this expression is substituted in Eq (9-17) (which is an approximate formula for compressible fluids), the familiar hydraulic formula is obtained (which is an exact formula for incompressible fluids)

$$V_{2 \text{ rev}} = \sqrt{\frac{2gH}{(1 - \beta^4)}} \quad (9-18a)$$

where  $H$  = differential *head* of flow in feet of fluid flowing

$g$  = local value of the acceleration of gravity

Here the *head* is defined as a height the height of a column of the given fluid that will produce an effect equivalent to that of a certain pressure

$$\frac{p_2}{p_1} = 1 - \frac{p_1 - p_2}{p_1} \quad \text{and let} \quad \frac{p_1 - p_2}{p_1} = x$$

Then

$$\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = (1 - x)^m \quad \text{where} \quad m = \frac{k-1}{k}$$

$$f(0) = 1 \quad f'(0) = -m \quad f''(0) = m(m-1) \quad f'''(0) = -m(m-1)(m-2)$$

Substituting in the series,

$$(1 - x)^m = 1 - mx + \frac{m(m-1)}{2} x^2 +$$

$$\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = 1 - \frac{k-1}{k} \left(\frac{p_1 - p_2}{p_1}\right) - \frac{k-1}{k} \frac{1}{2k} \left(\frac{p_1 - p_2}{p_1}\right)^2 +$$

In most cases the head is indirectly found by measuring the pressure with a manometer that uses a fluid other than the fluid flowing. When the pressure exerted by the system head is equated to that of the manometer (method is found in Table IX, Appendix),

$$\rho_1 H \frac{g}{g_c} = z_m (\rho_m - \rho_1) \frac{g}{g_c}$$

or

$$H = \frac{z_m (\rho_m - \rho_1)}{\rho_1} \quad (9-19)$$

where  $z_m$  = manometer reading (ft)

$\rho_m$  = density of fluid in manometer (lb<sub>m</sub>/ft<sup>3</sup>)

$\rho_1$  = density of fluid flowing (lb<sub>m</sub>/ft<sup>3</sup>)

Thus, from the manometer reading and Eq (9-19) the head can be calculated, with this value and Eq (9-18a) the velocity can be determined

**9-7 The Hydraulic Equation.** In many flow problems of compressible fluids the simple hydraulic equations will give good approximations to the correct answers. Such formulas can be obtained from the steady-flow energy equation

$$Q - W = J(u_2 - u_1) + (p_2 v_2 - p_1 v_1) + \left( \frac{V_2^2 - V_1^2}{2g_c} \right) + (z_2 - z_1) \frac{g}{g_c} \quad (3-13)$$

If this general equation is restricted to a system that does not involve heat or work or friction and the fluid in steady flow is incompressible, it will reduce to

$$p_1 v_1 + \frac{V_1^2}{2g_c} + z_1 \frac{g}{g_c} = \text{constant} \quad (9-20a)$$

$$\left[ \frac{\text{ft lb}_f}{\text{lb}_m} \right] + \left[ \frac{\text{ft lb}_f}{\text{lb}_m} \right] + \left[ \frac{\text{ft lb}_f}{\text{lb}_m} \right]$$

Equation (9-20a) and its derivatives can be called *Bernoulli's theorem*<sup>1</sup>. Each term has dimensions of energy

$$pv = \text{flow or pressure energy}$$

$$\frac{V^2}{2g_c} = \text{kinetic or velocity energy}$$

$$z \frac{g}{g_c} = \text{potential or height energy}$$

The equation can be changed to a different form by dividing each term by the specific volume

$$p_1 + \rho_1 \frac{V_1^2}{2g_c} + \rho_1 z_1 \frac{g}{g_c} = \text{constant} \quad (9-20b)$$

$$\left[ \frac{\text{lb}_f}{\text{ft}^2} \right] + \left[ \frac{\text{lb}_f}{\text{ft}^2} \right] + \left[ \frac{\text{lb}_f}{\text{ft}^2} \right]$$

<sup>1</sup> See also Eq (4-11), and Example 3, p 103

Here, each term has dimensions of pressure where

$$\begin{aligned} p &= \text{static pressure} \\ \rho \frac{V^2}{2g_c} &= \text{dynamic or velocity pressure} \\ \rho z \frac{g}{g_c} &= \text{elevation pressure} \end{aligned}$$

And if Eq (9-20b) is divided again by the specific weight  $\gamma$ , where

$$\gamma = \rho \frac{g}{g_c} \quad (\text{Example 6, Chap I})$$

then,

$$\frac{p_1}{\gamma_1} + \frac{V_1^2}{2g} + z_1 = \text{constant} \quad (9-20c)$$

$$[\text{ft}] + [\text{ft}] + [\text{ft}]$$

Here each term has dimensions of feet and therefore is a "head"

$$\begin{aligned} \frac{p}{\gamma} &= \text{static pressure head} \\ \frac{V^2}{2g} &= \text{dynamic or velocity head} \\ z &= \text{elevation head} \end{aligned}$$

Thus, Bernoulli's equation can be interpreted to state that either the total energy or the total pressure or the total head remains constant during a frictionless flow of an incompressible fluid in the absence of heat and work transfers. For this reason the word *head* is often used to designate any term in these three equations, although it should be precisely used only for terms with dimension of feet, such as those of Eq (9-20c)

**9-8. Reynolds' Criterion of Flow.** The *Reynolds number*,  $Re$ , is an important dimensionless parameter of fluid flow. Osborne Reynolds observed that the flow of fluids exhibits two characteristics. Under some conditions, annular elements of the fluid move in essentially straight paths parallel to the axis of the pipe with the greatest velocity at the center of the pipe and zero velocity for a very thin annular ring at the walls. The distribution of velocity across the pipe diameter is parabolic (Fig 9-4a). This type of motion is called *laminar*, *streamline*, or *viscous* flow. As the velocity of the fluid is increased, the fluid acquires a radial component with the appearance of eddies, and the flow is said to be *turbulent* (Fig 9-4b). In turbulent flow the velocity distribution tends to be uniform except at the walls, where the velocity must necessarily approach zero for a very thin boundary layer. For flow in pipes, the velocity distribution for turbulent flow is such that the average velocity is about 0.8 of the

maximum velocity For flow through a nozzle (Fig 9-4c) it can be safely assumed that the foregoing number approaches one

The transition from laminar to turbulent flow will depend on the  $Re$  as well as on the straightness of the channel and on the lack of disturbances to the flow, such as those created by rough walls or by fittings If the  $Re$  is below 2,200, only laminar flow will be present

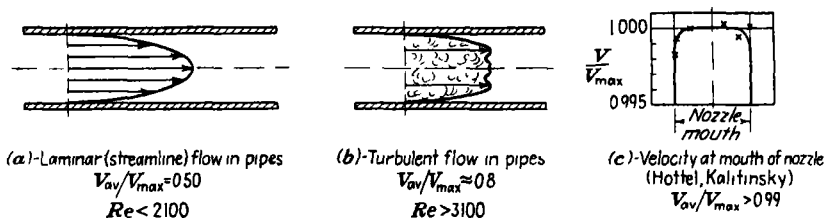


FIG 9-4 Velocity distribution diagrams

Above this value the flow can be assumed to be turbulent The  $Re$  can be evaluated by

$$Re = \frac{DV\rho}{\mu_f g_c} = \frac{DV\rho}{\mu_m} \quad (1-1)$$

If the mass flow is known, then from the continuity equation

$$m = \frac{AV}{v} = AV\rho$$

or

$$Re = \frac{1}{D} \frac{27m}{\mu_m} \quad (9-21)$$

where  $m$  = mass flow ( $\text{lb}_m/\text{sec}$ )

$D$  = diameter of round section (ft)

$\mu_f$  = viscosity ( $\text{lb}_f \text{ sec}/\text{ft}^2$ )

$\mu_m = \mu_f g_c$

$g_c$  = dimensional constant ( $32.17 \text{ lb}_m \text{ ft}/\text{lb}_f \text{ sec}^2$ )

**Example 6.** Calculate the  $Re$  for flow of air through an orifice of 1.820 in diameter at a rate of 1.173  $\text{lb}_m \text{ sec}^{-1}$ . The temperature of the air is 60 F

**Solution:** From Tables I and III, Appendix, the viscosity of air is

$$\mu_m = 0.0000121 \text{ lb}_m/\text{ft sec}$$

Hence,

$$Re = \frac{1}{D} \frac{27m}{\mu_m} = \frac{1}{1.820} \frac{27(1.173)}{0.0000121} = 815,000 \quad \text{Ans}$$

**Example 7:** Calculate the kinetic energy for laminar flow

**Solution:** In laminar flow the velocity distribution is parabolic, hence, at any radius the velocity is

$$V = V_{\max} \left( 1 - \frac{r^2}{R^2} \right)$$

The average velocity is defined by the continuity equation

$$m = \frac{AV_{\text{avg}}}{v} = \int_0^R dm$$

The mass passing through any annular ring at radius  $r$  is

$$\begin{aligned} dm &= \frac{(dA)V}{v} = \frac{(2\pi r dr) \left[ V_{\max} \left( 1 - \frac{r^2}{R^2} \right) \right]}{v} \\ m &= \frac{2\pi V_{\max}}{R^2 v} \int_0^R (R^2 - r^2) r dr \\ &= \frac{\pi V_{\max}}{2R^2 v} [-(R^2 - r^2)^2]_0^R \\ &= \frac{\pi R^2 V_{\max}}{2v} = \frac{AV_{\max}}{2v} \end{aligned}$$

But this equals

$$\frac{AV_{\text{avg}}}{v}$$

Hence,

$$V_{\text{avg}} = \frac{1}{2} V_{\max} \quad \text{and} \quad V = 2V_{\text{avg}} \left( 1 - \frac{r^2}{R^2} \right)$$

The kinetic energy is obtained by summing the kinetic energy for each annular ring

$$\begin{aligned} \text{KE} &= \int_0^R \frac{1}{2g_c} V^2 dm = \frac{8\pi V_{\text{avg}}^3}{g_c R^2 v} \int_0^R (R^2 - r^2)^2 r dr \\ &= \frac{\pi V_{\text{avg}}^3}{g_c R^2 v} [-(R^2 - r^2)^3]_0^R = \frac{\pi R^2 V_{\text{avg}}^3}{g_c v} \\ &= \frac{1}{g_c} m V_{\text{avg}}^2 \quad \text{Ans} \end{aligned}$$

Here it is seen that the kinetic energy for laminar flow is twice that computed by the usual assumption of uniform velocity. However, in most cases turbulent flow is present. In pipe lines where the velocity distribution results in an average velocity of 0.8 of the maximum it will be found that the kinetic energy is half again that computed by assuming a constant velocity. Hence, for preciseness the velocity distribution should be investigated, but this refinement is rarely necessary. For flow through nozzles, however, the kinetic energy will closely approach the usual figure of  $(1/2g_c)mV^2$ .

**9-9. The Ideal Mass Flow Rate for the Nozzle.** The most general equation for the ideal mass flow rate through the nozzle can be found

by combining the continuity equation with Eq (9-3):

$$m_{\text{rev}} = F_c A_2 \sqrt{\frac{2J g_c (h_1 - h_2)_{s=c}}{v_2^2}} \quad (9-22)$$

Equation (9-22) is valid for all fluids. By restricting the fluid to one that obeys, or approximately obeys, the laws governing perfect gases, equations can be obtained in terms of pressure, temperature, and specific volume. The continuity equation can be combined with Eq (9-5b) [in the manner followed in deriving Eq (9-6)]

$$m_{\text{rev}} = F_c A_2 \sqrt{\frac{2g_c k R T_1}{(k-1)v_1^2} \left[ (r_p)^{\frac{2}{k}} - (r_p)^{\frac{k+1}{k}} \right]_{s=c}} \quad (9-23a)$$

$$= F_c A_2 \sqrt{\frac{2g_c k p_1}{(k-1)v_1} \left[ (r_p)^{\frac{2}{k}} - (r_p)^{\frac{k+1}{k}} \right]_{s=c}} \quad (9-23b)$$

And if still more approximations are permissible, the expanded forms of the velocity equations [Eqs (9-15a) and (9-17)] can be used

$$m_{\text{rev}} = F_c A_2 \sqrt{\frac{2g_c p_1 r_p^{\frac{2}{k}}}{v_1} \left[ \frac{p_1 - p_2}{p_1} + \frac{1}{2k} \left( \frac{p_1 - p_2}{p_1} \right)^2 \right]} \quad (9-24)$$

$$m_{\text{rev}} = F_c A_2 \sqrt{\frac{2g_c (p_1 - p_2)}{v}} \quad (9-25)$$

$m$  = mass flow rate (lb<sub>m</sub>/sec)

$F_c$  = correction factor for velocity of approach

$A$  = area (ft<sup>2</sup>)

$R$  = specific gas constant  $\left( \frac{1,545 \text{ ft lb}_f}{M \text{ lb}_m \text{ R}} \right)$

$r_p$  = pressure ratio at section 2

$T$  = temperature (R)

$p$  = pressure (lb<sub>f</sub>/ft<sup>2</sup>)

$v$  = specific volume (ft<sup>3</sup>/lb<sub>m</sub>)

$h$  = enthalpy (Btu/lb<sub>m</sub>)

$g_c$  = dimensional constant  $\left( 32.17 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2} \right)$

Which of these equations should be used in solving a particular problem will depend on a number of conditions

- 1 The accuracy in measuring pressure and temperature,
- 2 The accuracy in calculating the specific volume (compressibility data should be used),



3. The accuracy of the assumption that the perfect-gas laws are adequate;
- 4 The accuracy of assigning to  $k$  a constant value,
- 5 The permissible error in the answer

Of course, whenever possible, Eq (9-22) should be used, but, even then, results may be encountered that are not as yet anticipated (Art 9-17) Note that, when a slide rule is used for computations, Eq (9-24) may be more accurate than Eq (9-23) Equation (9-25) is best used as a first approximation to the answer

Since the mass flow is constant throughout the nozzle, it is convenient to select the throat to be the section designated by the subscript 2, if only because the dimensions and the pressure at the throat of a nozzle are more easily measured or computed than at other sections <sup>1</sup>

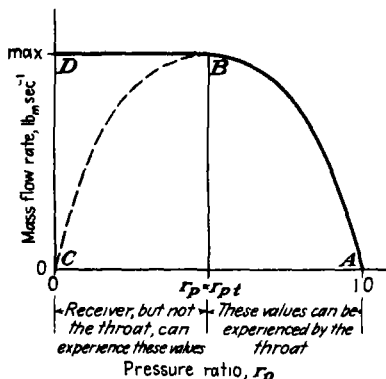


FIG 9-5 Variation of mass flow rate with throat pressure ratio for nozzle or venturi

For note that Eq (9-23a) differs from Eq (9-6) only by the area factor  $A_2$ , and therefore the critical pressure ratio found for Eq (9-7) or (9-8) applies as well to Eq (9-23) Because of this, when the pressure at the throat reaches the minimum pressure of the critical ratio, not only does the velocity remain constant for any additional decrease in exit pressure but the mass flow rate also remains constant. This constancy of throat conditions is illustrated in Fig 9-3 for here the over-all pressure ratios for tests C, D, and E are different,

although the throat pressure ratios are the same and therefore the mass flow rates for all three tests must be equal

In test A (and probably test B) the mass flow rate will be less than that of the others, for here the minimum throat pressure has not been reached and therefore the velocity at the throat has not attained its maximum value

In Fig 9-5 the mass flow rate is shown plotted against the pressure ratio at the throat of the nozzle If the mass flow rate is calculated from Eq (9-23) for assumed throat values of  $r_p$  from one to zero, note that the curve ABC results and, if  $p_t$  approached zero, the flow would

<sup>1</sup> And, invariably, the correction factor is based upon the throat diameter

also approach zero. But since  $p_t$  can never fall below the critical pressure, the decrease from  $B$  to  $C$  is unreal and the actual flow rate is shown by curve  $ABD$ .

**9-10. The Actual Mass Flow Rate for the Nozzle.** A *coefficient of discharge* is defined as the ratio of the actual mass rate of flow to the ideal rate of flow that theoretically could be attained by a reversible expansion from the initial state to the final state:

$$C = \frac{\text{actual mass rate of flow}}{\text{ideal mass rate of flow}} = \frac{m_{\text{actual}}}{V_{\text{isen}} A / v} \quad (9-26)$$

The actual flow rate is found by test while the ideal flow rate is calculated by one of the equations in Art 9-9. In this manner the coefficient of discharge and the variations in the coefficient that will accompany any change in operating conditions are determined. If sufficient data of this kind are available, then it is possible to predict the value of the coefficient of discharge for a test and therefore find, quite simply, the mass flow rate. For the ideal rate determined by one of the equations in Art 9-9 can be multiplied by the coefficient of discharge to yield the actual rate.

Equations (9-22) and (9-23) are often referred to as adiabatic equations (although the precise term *isentropic* would be a better name), and for this reason the discharge coefficients for these equations are called *adiabatic coefficients of discharge*. Equation (9-25) is the well-known hydraulic formula, and therefore its discharge coefficient is called a *hydraulic* or a *water* coefficient of discharge.

The factors influencing the coefficients of discharge are discussed in following articles.

**Example 8** Determine the dimensions for a nozzle that is to expand  $1 \text{ lb}_m \text{ sec}^{-1}$  of steam from  $p_1 = 100 \text{ psia}$  and  $t_1 = 600 \text{ F}$  to  $p_2 = 20 \text{ psia}$  if the coefficient of discharge is 0.98 and velocity of approach is negligible. (Data are basically the same as for Examples 1 and 4.)

**Solution:** Equation (9-22), corrected with a discharge coefficient, is applicable

$$m = CF_1 \sqrt{\frac{2Jg_c(h_1 - h_2)_{\text{isen}}}{v_2^2}}$$

At the throat (data from Example 1)

$$\begin{aligned} p_t &= 54.6 \text{ psia} \\ (\Delta h)_{\text{isen}} &= 64.1 \text{ Btu/lb}_m \\ v_{t \text{ isen}} &= 984.4 \text{ ft}^1/\text{lb}_m \end{aligned}$$

When these values are inserted in Eq (9-22)

$$10 = 0.98 A_1 \sqrt{\frac{2(32.17)(778)(64.1)}{(9.844)^2}}$$

$$A_1 = 0.0056 \text{ ft}^2 \quad \text{Ans}$$

(Compare with Examples 1 and 4)

In similar manner the area at the mouth of the nozzle can be found (data from Example 1)

$$10 = 0.98 A_2 \sqrt{\frac{2(32.17)(778)(154.3)}{(21.279)^2}}$$

$$A_2 = 0.00783 \text{ ft}^2 \quad \text{Ans}$$

(Compare with Examples 1 and 4)

**9-11. Standards for the Venturi and the Flow Nozzle.** In many applications the measuring device is a permanent part of an industrial

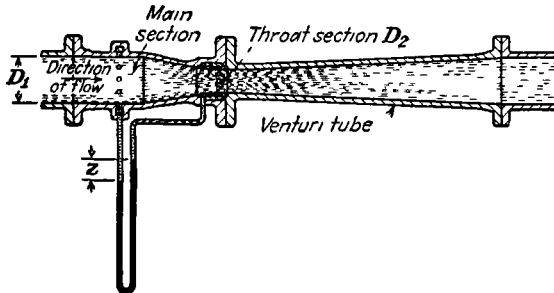


FIG 9-6 Venturi

system, therefore, the device should not introduce a loss, for a loss will cause an additional expense in pumping costs. For this reason the venturi is preferred as a means for measuring flow and is the standard meter for water or steam flows in many industrial applications. In Fig 9-6 a venturi and manometer are illustrated. The venturi is made of cast iron or steel, with bronze or monel linings to minimize corrosion. Most styles use a piezometer ring or annular space at both the inlet and throat communicating with the flow chamber by a series of radially drilled holes. This construction ensures that the average pressure is being measured, and it also acts as a safety factor against the possibility of one hole becoming plugged. The approach to the throat is a frustrum of a cone with angle of 25 to 30 deg, the diameter of the throat being one-fourth to one-half of the pipe diameter, and the length being one-half of its own diameter. The downstream section or diffuser is a cone with angle of 7 deg or less. The over-all loss in pressure can be estimated to be roughly 10 per cent of the differential

pressure. Figure 9-7 illustrates the variation of the coefficient of discharge for different sizes of venturi. The size is given by stating the pipe diameter and throat diameter. The coefficient of discharge is

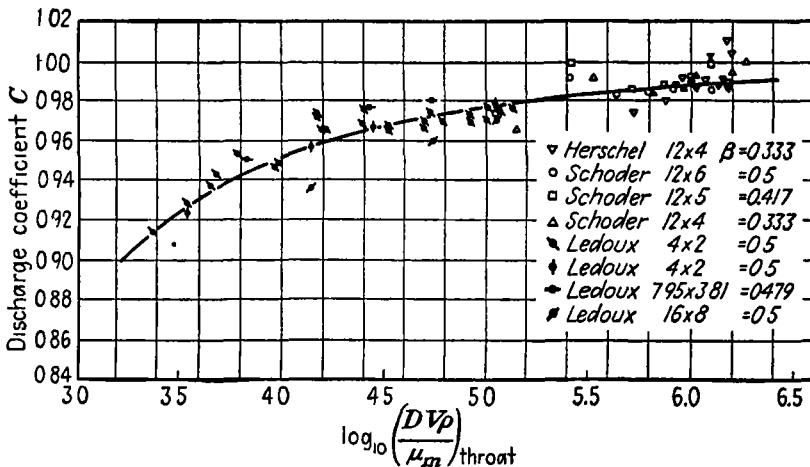


Fig 9-7 Venturi discharge coefficients (from reference 1)

affected mainly by the Reynolds number, and for high  $Re$ , that is, highly turbulent flow conditions, a value of 0.98 can be used as an approximate value

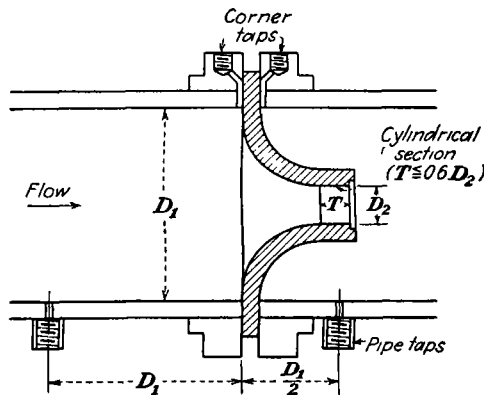


Fig 9-8 Long-radius flow nozzle

A flow nozzle consists of a short cylinder with one end flared to form the entrance to the nozzle (Fig 9-8). The purpose of the cylindrical throat is to ensure that the fluid will leave the nozzle without contraction in order that the area of the throat and the jet may be considered

equal In effect, the flow nozzle is a venturi without a diffuser; hence, the loss of head from failure to recompress the high-velocity flow may vary from 30 to 90 per cent of the differential. These values correspond to values of  $\beta$  from 0.8 to 0.2

Two types of pressure connection are in use, corner taps and pipe wall taps, as illustrated in Fig 9-8 The manometer differential for the corner taps will be slightly higher than that for the pipe taps because of the pressure build-up from impact at the corner location, hence, the coefficient of discharge will be slightly lower For either type of connection, unless high accuracy is desired, the coefficient of

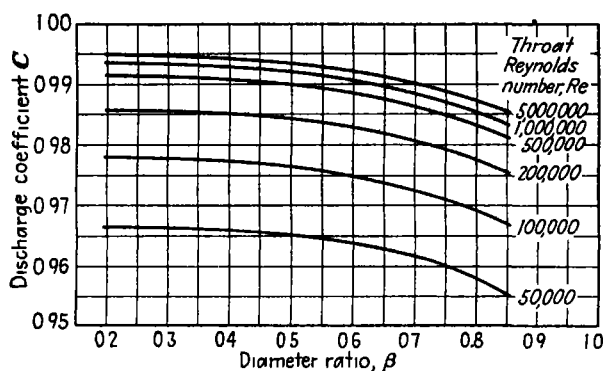


FIG 9-9 Discharge coefficients of long-radius flow nozzles \*

discharge can be selected from Fig 9-9 \* (And for best accuracy, consult Reference 7)

**9-12. Standards for the Orifice.** Probably the oldest device for measuring the mass flow rate is the thin plate orifice constructed in the manner of Fig 9-10 The orifice is installed with the sharp edge on the upstream side and beveling, if any, on the downstream side. The pressure in front of the orifice may be slightly higher than the true pressure because of impact. In passing through the orifice the pressure drops abruptly, reaching a minimum value at the *vena contracta* or location of smallest jet diameter At this point all filaments of the flow become parallel Beyond this point the pressure increases as the fluid is decelerated, and this action is accompanied by considerable turbulence from lack of a diffuser section Hence, the downstream pressure is

\* BEAN, H S, S R BEITLER, and R E SPRENKLE Discharge Coefficients of Long Radius Flow Nozzles, *Trans ASME*, **63** (No 5), 439-445 (July, 1941)

(Although Fig 9-9 is for 2-in pipe with pipe wall taps, it can be used without significant error for other pipe sizes)

considerably lower than for a venturi and of the same order as for a flow nozzle

Inspection of Fig 9-10 indicates that the pressure differential measured on a manometer will be influenced by the location of the pressure taps with respect to the orifice. Figure 9-11 shows the standard dimensions for locating the various types of pressure taps. The *vena contracta* taps will give the highest differential pressure and this ensures best accuracy. However, the inconvenience exists of locating the section of minimum pressure. Plate and corner taps allow the openings to be made in the orifice plate that can be inserted into the pipe line at any convenient flanged joint without the necessity of drilling and tapping the line.

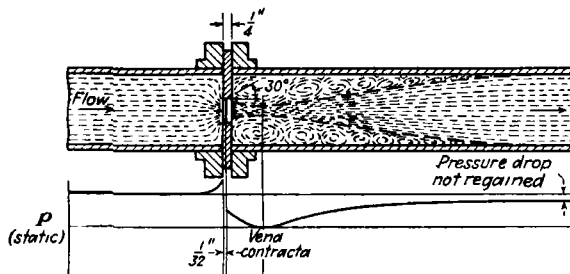


FIG 9-10 Flow through thin-plate sharp-edged orifice

In flowing through the orifice plate, the jet contracts to an area of about 0.6 that of the orifice, and therefore the flow coefficient, which is based upon the orifice area, is much less than unity. The orifice must be carefully constructed if predetermined discharge coefficients are to be used without a calibration test because, for example, rounding of the inlet corner will decrease the jet contraction, thus increasing the real flow area and therefore increasing the quantity of flow. The mass flow rate can be predicted by the adiabatic (so-called) formulas [Eqs (9-22), (9-23), and (9-24)] if the "adiabatic" coefficient of discharge is found by calibration. This coefficient, however, will vary markedly with change in flow conditions. Moreover, the phenomenon of the critical ratio does not appear for sharp-edged orifices, or else it is obscured by changes in the low discharge coefficient, because experiments show that the mass flow rate continues to increase as the pressure ratio is decreased below the critical (Fig 9-17a).

**Example 9.** Air is flowing through a 6-in. pipe and is metered by a 1/820-in. thin plate orifice with flange taps. The "adiabatic" coefficient of discharge from calibration tests is 0.68, and the manometer depression is 20 in. Hg. The upstream temperature of the fluid is 60 F, and the pressure is 30 psia. Compute the flow rate.

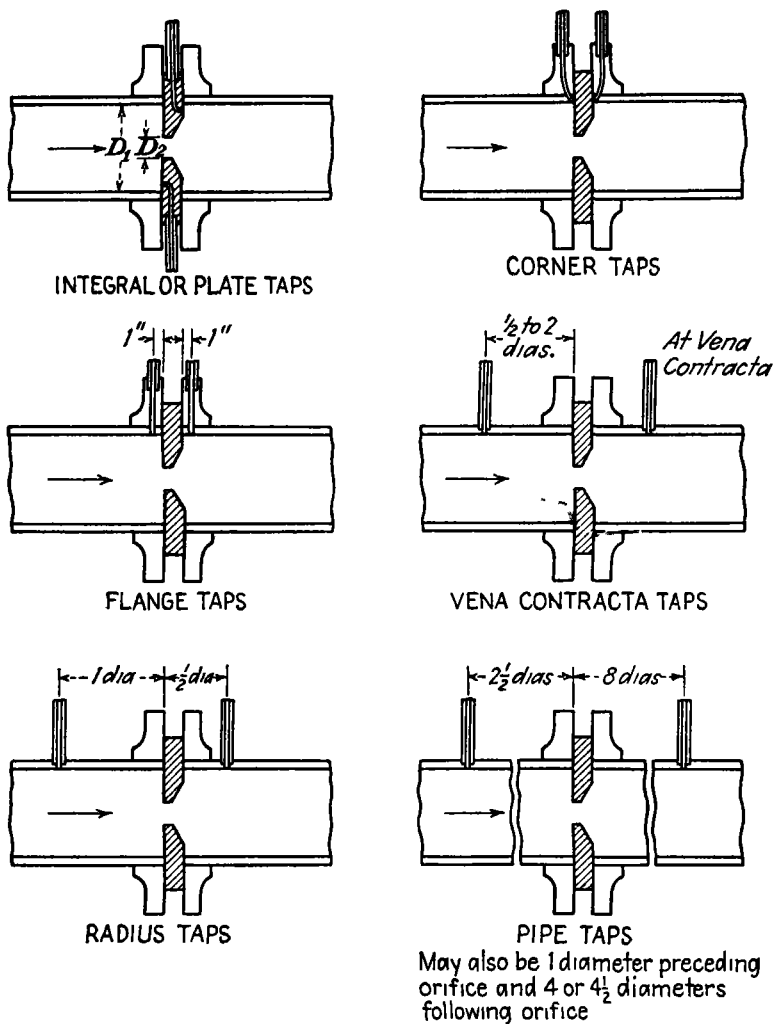


FIG 9-11 Locations for orifice taps (Diameter refers to upstream pipe)

**Solution.** The specific gravity of mercury is 13.59, and by Table IX (Appendix)

$$\begin{aligned}
 (p_1 - p_2)_{\text{PM}} &= 0.03609 z_m G \frac{g}{g_c} \\
 &= (0.03609)(20)(13.59) \\
 &= 9.82 \text{ psi} \\
 r_p &= \frac{p_2}{p_1} = \frac{20.18}{30} = 0.672
 \end{aligned}$$

The diameter ratio  $\beta$  is

$$\beta = \frac{D_2}{D_1} = \frac{1\ 820}{6\ 065} = 0\ 3$$

where the inside diameter<sup>1</sup> of the pipe is used, and not the nominal size. The specific volume of air for this low pressure can be found by the perfect-gas equation

$$v_1 = \frac{RT}{p_1} = \frac{1545(520)}{30(144)} = 6\ 41\ \text{ft}^3/\text{lb}_m$$

When these values are substituted along with  $k = 1\ 4$  in Eq. (9-23b), with a coefficient of discharge  $C$ ,

$$\begin{aligned} m &= CA_2 F_c \sqrt{\frac{2g_c k}{(k-1)} \frac{p_1}{v_1} \left[ r_p^{\frac{2}{k}} - r_p^{\frac{k+1}{k}} \right]} \\ &= 0\ 68 \left( \frac{\pi(1\ 820)^2}{4(144)} \right) \frac{1}{\sqrt{1 - (0\ 3)^4} (0\ 672)^{1\ 43}} \sqrt{\frac{64\ 4(1\ 4)30(144)}{(0\ 4)6\ 41} (0\ 672^{1\ 43} - 0\ 672^{1\ 713})} \\ &= 1\ 173\ \text{lb}_m/\text{sec} \quad \text{Ans} \end{aligned}$$

In measuring the flow of gases in large ducts, thin plate orifices are used either in the duct itself or at the inlet or discharge end. Duct orifices must be preceded and followed by considerable lengths of straight pipe, for this reason, either inlet or discharge orifices are preferable. The orifice<sup>2</sup> is made from a plate  $\frac{1}{8}$  to  $\frac{3}{8}$  in. in thickness without chamfer or bevel on the downstream side, and sharp-edged on the upstream side. It matters not whether a corner or a flange tap is used.

A coefficient of discharge of 0.60 can be used for routine calculations with Eq. (9-25) for either inlet or discharge orifices.

**9-13. Factors Affecting Flow Measurements.** Proper installation of the flow metering device requires that the element be far removed from fittings, valves, or changes in direction of the piping that will cause disturbances to be created in the flow. Specific rules<sup>3</sup> for all types of installations are many, a fairly safe rule is to ensure that the metering element is preceded by a length of thirty diameters and followed by a length of four diameters of straight pipe. When difficulty is experienced in meeting these requirements, straightening vanes (Fig. 9-12) can be used, located a distance of at least ten pipe diameters upstream from the element.

<sup>1</sup> There are over twenty different inside dimensions for the 6-in. nominal pipe size.

<sup>2</sup> MARKS, L. S. Square-edged Inlet and Discharge Orifices, *Trans. ASME*, **58** (No. 8), 593-597 (November, 1936).

<sup>3</sup> SPRENKLE, R. E. Piping Arrangements for Acceptable Flowmeter Accuracy, *Trans. ASME*, **67** (No. 5), 345-360 (July, 1945).



If the flow is pulsating, means must be devised to eliminate the uneven flow before the fluid reaches the primary element, or considerable error will be present. One method is to introduce into the line a receiver or tank preceded and followed by throttling orifices to damp out the pulsations. The existence of pulsations in the line

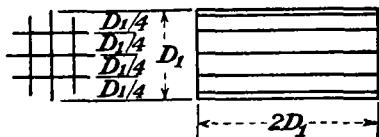


FIG 9-12 Straightening vanes

can be determined by an indicator (Art 4-5)

**9-14 ASME Fluid Meters Report.<sup>1</sup>** The bible on fluid flow for the mechanical engineer is the Fluid Meters report of the ASME. Here are listed the coefficients of discharge and the procedures to be followed in accurately measuring a flow rate of either gases or liquids. Since the engineer turns to this report whenever a discharge coefficient must be assumed, it will be well to examine the form of presentation. The ASME proposes as a general equation for the flow nozzle and venturi the relationship

$$m = 0.525 K \phi D_2^2 \sqrt{\rho_1(p_1 - p_2)} \quad (9-27)$$

where  $m$  = mass flow rate ( $\text{lb}_m \text{ sec}^{-1}$ )

$K$  = combined discharge and approach factor coefficient

$\phi$  = "adiabatic" expansion factor

$D_2$  = diameter of throat (in)

$\rho_1$  = upstream density of fluid ( $\text{lb}_m \text{ ft}^{-3}$ ) computed from compressibility data

$(p_1 - p_2)$  = differential pressure across element ( $\text{lb}_f \text{ in}^{-2}$ )

A rational development of Eq (9-27) can be made from Eq (9-23b) corrected by a discharge coefficient  $C$

$$m = C F_c A_2 \sqrt{\frac{2g_c k p_1}{(k-1)v_1} \left[ (r_p)^{\frac{2}{k}} - (r_p)^{\frac{k+1}{k}} \right]_{s-c}}$$

This expression can be rearranged into several parts for similarity with Eq (9-27) (the expanded value of the correction factor is inserted)

$m =$

$$\underbrace{\frac{\sqrt{2g_c} \pi (12)}{4(144)}}_{0.525} \underbrace{\frac{C}{\sqrt{1-\beta^4}}}_{K} D_2^2 \underbrace{\left[ r_p^{\frac{2}{k}} \left( \frac{k}{k-1} \right) \left( \frac{1-r_p}{1-r_p} \right) \left( \frac{1-\beta^4}{1-\beta^4 r_p^{\frac{k}{k-1}}} \right) \right]^{\frac{1}{2}}}_{\phi} \underbrace{\frac{\sqrt{\rho_1(p_1-p_2)}}{\sqrt{\rho_1(p_1-p_2)}}}_{(9-28)}$$

Here it is recognized that the mass flow depends upon a flow coefficient  $K$ , an expansion coefficient  $\phi$ , and the hydraulic formula  $\sqrt{\rho_1(p_1-p_2)}$ .

<sup>1</sup> See references 1 and 7.

When a liquid is metered through a well-formed venturi or flow nozzle,  $\phi$  will be 1.0 because no expansion occurs, and  $K$  can be computed from the measured mass flow. Thus,  $K$  is found to be a function of  $D$ ,  $Re$ , and  $\beta$ . Now when a compressible fluid is metered with the same primary element, the only change that will occur will be that the fluid will expand. The expansion will be at all times guided by the area of the nozzle. Hence, a nozzle coefficient  $C$  (or  $K$ ), determined by a relatively simple test on a liquid such as water, can be modified by the factor  $\phi$  to predict the mass flow of a compressible fluid. That this reasoning is correct has been proved by test.

For the square-edged orifice, the expansion factor  $\phi$  cannot be calculated from Eq. (9-28) because a compressible fluid will expand both longitudinally and transversely from lack of control of the expansion process. The general equation for the orifice is similar to Eq. (9-27)

$$m = 0.525KY_1D_2^2 \sqrt{\rho_1(p_1 - p_2)} \quad (9-29)$$

Here the factor  $Y_1$  replaces  $\phi$ , values of  $Y_1$  are determined by experiment.

The Fluid Meters report lists values of  $K$  for flange, *vena contracta*, and pipe taps for different pipe sizes. One of these tables is reproduced as Table 9-2, note

TABLE 9-2—FLANGE TAPS\*

Values of the Flow Coefficient  $K$ , Velocity-of-approach Factor Included, for Various Sizes of Pipe and at Reynolds Numbers  $Re$  Corresponding to the Headings of the Different Columns

For 6-in. Pipe

$\beta$	25,000	50,000	100,000	150,000	250,000	500,000	1,000,000	10,000,000
0 100	0 6018	0 5973	0 5950	0 5942	0 5936	0 5932	0 5929	0 5927
0 200	0 6061	0 6008	0 5981	0 5972	0 5965	0 5959	0 5957	0 5954
0 250	0 6082	0 6029	0 6002	0 5994	0 5987	0 5981	0 5978	0 5976
0 300	0 6107	0 6055	0 6028	0 6020	0 6013	0 6007	0 6004	0 6002
0 400	0 6209	0 6145	0 6113	0 6103	0 6095	0 6089	0 6085	0 6082
0 500	0 6430	0 6328	0 6276	0 6260	0 6246	0 6236	0 6231	0 6226
0 600	0 6836	0 6658	0 6569	0 6540	0 6515	0 6498	0 6488	0 6481
0 700	0 7500	0 7199	0 7048	0 6998	0 6958	0 6938	0 6913	0 6899
0 750	0 8017	0 7616	0 7417	0 7348	0 7294	0 7255	0 7235	0 7217

\* Abstracted from reference 1

that the values for  $K$  are plotted against  $Re$ , a number with value determined by  $m$ , which is unknown. To solve a flow problem, the  $Re$  must be assumed,  $K$  found from the table, and  $m$  calculated by Eq. (9-29). This trial method is not difficult because the values for  $K$  do not change rapidly with change of  $Re$ .

Experimental values for  $Y_1$  are shown in Fig. 9-13, for liquids  $Y_1 = 1.0$ .

**Example 10:** Suppose in Example 9 that the "adiabatic" coefficient were unknown. Determine the flow rate and compare the coefficient of discharge with that of Example 9.

**Solution:** Assume for the first trial that  $Re$  is 500,000 By Table 9-2 and Fig 9-13 for values of  $\beta = 0.3$ ,  $r_p = 0.672$ ,

$$K = 0.6007$$

$$Y_1 = 0.91$$

When these values are substituted in Eq (9-29),

$$m = 0.525 K Y_1 D_2^2 \sqrt{\rho_1 (p_1 - p_2)}$$

$$= 0.525 (0.6007) (0.91) (3.31) \sqrt{0.156 (9.82)}$$

$$= 1.173 \text{ lb}_m/\text{sec} \quad \text{Ans}$$

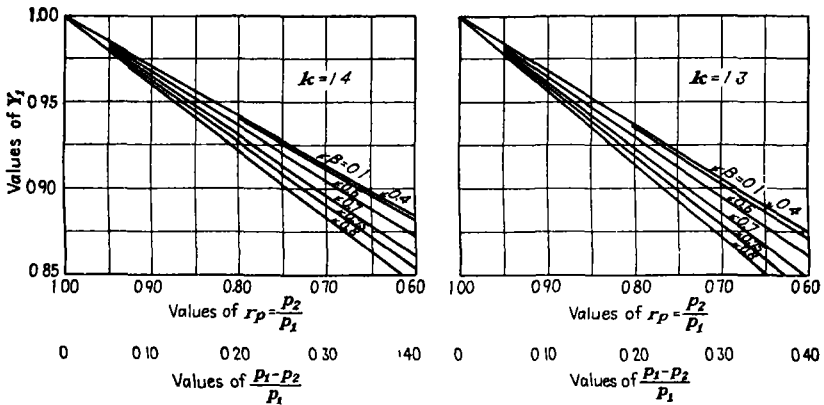


FIG 9-13 Values of the experimental expansion factor  $Y_1$  for orifices (flange, radius, and vena contracta taps) (from reference 1)

From Eq (9-28)

$$K = \frac{C}{\sqrt{1 - \beta^4}}$$

$$C = 0.6007 \sqrt{1 - 0.0081}$$

$$C_{\text{hyd}} = 0.600 \quad \text{Ans}$$

compared with

$$C_{\text{adia}} = 0.68$$

Coefficients calculated by the ASME method do not vary over as wide limits as do the adiabatic coefficients

**9-15. Temperature of a Moving Stream.** The true temperature of a moving fluid is the temperature that would be shown by a measuring instrument moving at the same speed as the fluid. However, the practical measurement of temperature is accomplished by instruments that are at rest relative to the fluid, and the mass-flow impact on the measuring device will give a higher reading of temperature than the true reading.

Theoretically, the kinetic energy of the moving fluid could be utilized to compress isentropically the fluid to a state of higher pressure,

higher temperature, and zero velocity. The temperature at this state of zero velocity is called the *stagnation temperature* or *total temperature*. Note that for gases that follow the perfect-gas relationships the stagnation temperature can be attained without isentropic compression. For by the First Law, applied to an adiabatic process in the absence of work, the change in kinetic energy of a stream is equal to the change in enthalpy; and the enthalpy of a perfect gas is a function only of temperature.

A temperature measuring device in a high-velocity stream will cause the fluid directly in front of the obstacle to be more or less isentropically compressed with attainment of a temperature that would approach the stagnation temperature. However, the thermal meter may not approximate the true stagnation temperature because a number of other factors will intervene. For example, there will be a radiation loss from the hotter thermometer to the colder gas and walls, frictional effects of the fluid flow on the indicator will be affected by the properties of the fluid, such as its viscosity, while the shape and relative position in the fluid stream will also enter the problem. For these reasons the measured temperature may be greater or less than the stagnation temperature. The *recovery factor* of the measuring device is defined as

$$\lambda = \frac{T_{\text{indicated}} - T_{\text{static}}}{T_{\text{stagnation}} - T_{\text{static}}} \quad (9-30)$$

For air and most gases the recovery factor is less than one. Twisted wire thermocouples in air have recovery factors<sup>1</sup> of 0.73–0.84. The higher values are obtained by axial flow over the couple and the lower values are for transverse flow.

For high velocities, probes are used to assist in the deceleration of the fluid and to guard against radiation errors. In Fig. 9-14 is illustrated<sup>1</sup> a probe for high-velocity stream measurements for conditions where the stream temperature and wall temperature are of the same order. In this probe, the high-velocity fluid is brought essentially to rest and the temperature measured by the thermocouple. Bleed holes allow a small but continuous flow past the thermocouple.

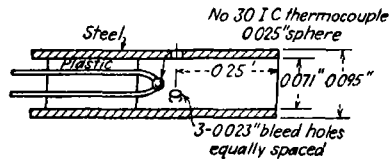


FIG. 9-14 Total temperature probe (Pratt and Whitney design)

<sup>1</sup> HOTTEL, H. C., and A. KALITINSKY, Temperature Measurements in High Velocity Air Streams, *J. Applied Mechanics*, 12 (No. 1), A25–A32 (March, 1945)

Radiation losses are negligible because of the shielding effect of the enclosed tube, which also acts as a diffuser. Recovery factors of 0.98 are reported for this probe for velocities under and slightly over the acoustic velocity.

The problem is more complicated if the temperature of the fluid is high compared with that of the wall, for radiation losses will increase considerably. To reduce such losses, multiple shields must be used as illustrated<sup>1</sup> in Fig. 9-15. This design, however, is for low-velocity work, and conditions of high velocities and high temperatures would necessitate a combination of the two designs (Figs. 14 and 15).

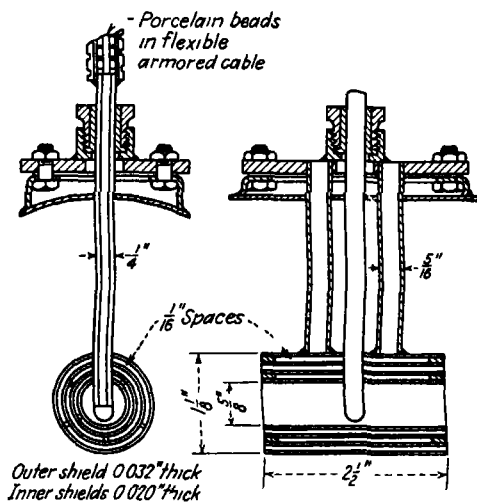


FIG. 9-15 Shielded thermocouple

**9-16. Pressure of a Moving Stream.** The true static pressure of a fluid in motion is relatively easy to measure compared with the true static temperature. Either a piezometer ring or a small radial hole into the pipe line will enable the pressure to be measured. However, the hole must be so located that no opportunity exists for impact, or a high pressure will be encountered. If the flow is pulsating, standing waves of pressure variations may exist and different static pressures will be experienced along the length of the pipe.

The *stagnation*, *total*, or *impact pressure* is the pressure that could be theoretically attained by utilizing the kinetic energy of the fluid to compress isentropically the fluid to a state of higher temperature.

<sup>1</sup> KING, W. J., Measurement of High Temperatures in High-Velocity Gas Streams, *Trans. ASME*, **65** (No. 5), 421-431 (July, 1943).

(stagnation), higher pressure, and zero velocity. The impact pressure is measured with a pitot tube; two styles are illustrated in Fig 9-16. In Fig 9-16a only the impact pressure is read and the static pressure is measured separately. This is the best method because the static pressure can be measured at a location preceding the pitot tube, and therefore disturbances in the flow stream created by the instrument are avoided. In Fig 9-16b both static and impact pressures are measured by openings on the instrument. If these two pressures are

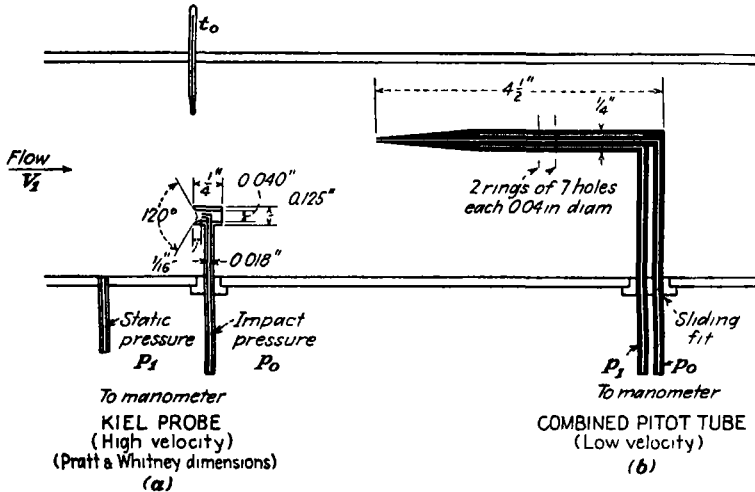


FIG 9-16 Pitot tubes

communicated to separate legs of the manometer, the difference is that pressure due to *velocity* or the *dynamic* pressure.

The fluid directly in front of the pitot tube can be considered to be isentropically compressed while its velocity becomes zero. The impact pressure at the tip of the tube can be computed on this assumption. The action is the direct opposite of expansion from a region of zero velocity; hence, Eqs (9-5b), (9-15a), (9-16a), and (9-18a) can be transformed to this inverse case

$$V_{1,\text{rev}} = \sqrt{\frac{2g_c k R T_0}{k-1} \left[ 1 - \left( \frac{p_1}{p_0} \right)^{\frac{k-1}{k}} \right]} \quad (9-5c)$$

$$= \sqrt{2g_c R T_0 \left[ \frac{p_0 - p_1}{p_0} + \frac{1}{2k} \left( \frac{p_0 - p_1}{p_0} \right)^2 \right]} \quad (9-15b)$$

$$= \sqrt{2g_c R T_0 \left( \frac{p_0 - p_1}{p_0} \right)} \quad (9-16b)$$

$$= \sqrt{2gH} \quad (9-18b)$$

where  $V_1$  = velocity approaching pitot tube (ft/sec)

$p_1$  = static pressure in pipe

$p_0$  = impact pressure

$H$  = differential head of flow (ft)

$T_0$  = temperature in region defined by  $p_0$  (R)

$R$  = gas constant  $\left( \frac{1,545 \text{ ft lb}_f}{M \text{ lb}_m \text{ R}} \right)$

It would appear that there are two unknowns  $V_1$  and  $T_0$  if  $p_0$  and  $p_1$  are measured with an impact tube and a pressure gauge. However, the temperature shown by the thermometer in Fig 9-16 will be  $T_0$  if the recovery factor is 1.0, or the stagnation temperature can be calculated if the recovery factor is known.

The value for velocity determined by the impact tube should be modified by a coefficient known as the *instrument factor*. This factor cannot be called a coefficient of discharge, for no flow passes through the impact tube. For low-velocity work the instrument factor can be considered to be 1.0. The instrument should be mounted parallel to the pipe and at least thirty pipe diameters from fittings.

For velocities above the acoustic, a compression shock may and probably will occur at the entrance to the tube, and the supersonic velocity is irreversibly reduced to a subsonic value. The subsequent compression as the velocity is reduced to zero does not reach the true stagnation pressure, which can be attained only by an isentropic compression. Hence, in most cases the pitot tube is used for velocities below the acoustic velocity.

The velocity determined with a pitot tube is a point velocity, and a traverse of the pipe must be made to find the variation of velocity across a diameter. An average velocity is determined by dividing the pipe into a number of equal annular areas and finding the average velocity of each area. The average velocity for the pipe is the average of the resulting numbers. Note that this is not an average of the pitot tube reading, for the readings are related to the square of the velocity.

In the case of a circular duct it is customary to divide the cross section into one central area and four concentric rings each of equal area. By placing the pitot tube at the mean radius of each of these areas, the velocity pressure for that area is found. The locations<sup>1</sup> of these points in a duct of radius  $R$  are  $0.316R$ ,  $0.548R$ ,  $0.707R$ ,  $0.837R$ , and  $0.949R$ . It is better practice to take these readings on both sides of the center line of the duct; thus, there are 10 readings in all, giving

<sup>1</sup> Consider that 10 equal areas are desired to be established in a circular duct

rise to the descriptive name *ten-point method*. For some work two traverses are made at right angles to each other, and thus there are 20 readings

**Example 11:** A 4-ft diameter duct carrying air of density 0.0736 lb<sub>m</sub>/ft<sup>3</sup> is traversed by a pitot tube using the ten-point method. The readings in inches of water at 72 F from one side of the duct to the other are, respectively, 0.210, 0.216, 0.220, 0.219, 0.220, 0.220, 0.218, 0.219, 0.220, and 0.216. Find the average velocity and the mass flow (local  $g = g_0$ )

**Solution:** The velocity at each point can be calculated and then averaged, but it is quicker to average the square roots of the readings

$$\sqrt{z_m} = \frac{\sqrt{0.210} + \sqrt{0.216} + \sqrt{0.216}}{10} = 0.4668$$

The densities of water and air are

$$\rho_m = 62.3 \text{ lb}_m/\text{ft}^3$$

$$\rho_1 = 0.0736 \text{ lb}_m/\text{ft}^3$$

$$\text{Mean } z_m = 0.216 \text{ in } \text{H}_2\text{O}$$

By Eq. (9-19)

$$\begin{aligned} H &= \frac{z_m(\rho_m - \rho_1)}{\rho_1} = \frac{0.216(62.3 - 0.074)}{(12)(0.074)} \\ &= 15.1 \text{ ft of fluid flowing} \end{aligned}$$

By Eq. (9-18b) (if  $g = g_0$ )

$$V = \sqrt{2gH} = \sqrt{64.4(15.1)} = 31.2 \text{ ft/sec} \quad \text{Ans}$$

while by the continuity equation

$$m = \frac{AV}{v} = \frac{\pi}{4} (4^2)(31.2)(0.0736) = 29 \text{ lb}_m/\text{sec} \quad \text{Ans}$$

**9-17. The Metastable Flow of Fluids.** Whenever a fluid passes over a phase boundary, it is usual to assume that a phase change occurs at the same instant. However, if the passage of the fluid over the phase boundary is swift, the phase change may be delayed, and a

of radius  $R$ . Then,

$$\pi r_1^2 = \pi(r_2^2 - r_1^2) = \pi(r_3^2 - r_2^2) \quad \pi(R^2 - r_3^2)$$

If these areas are equal,

$$r_2^2 = 2r_1^2 \quad r_3^2 = 3r_1^2 \quad R^2 = 10r_1^2$$

Therefore,

$$r_1 = \frac{1}{\sqrt{10}} R \quad r_2 = \frac{\sqrt{2}}{\sqrt{10}} R \quad r_3 = \frac{\sqrt{3}}{\sqrt{10}} R \quad r_4 = \frac{\sqrt{4}}{\sqrt{10}} R \quad \text{etc}$$

And now radii  $r_1, r_2, r_3$ , etc., are the mean values for five equal areas

$$r = 0.316R, 0.548R, 0.707R, \text{ etc}$$



metastable state may be attained. For example, if steam is expanded in a nozzle from the vapor region to the two-phase region, at some stage of the expansion the saturation line will be crossed and, at the same instant, the steam should begin to condense. However, tests show that the condensation may be delayed until some lower temperature and pressure are attained before a sudden condensation occurs in the form of a vast number of extremely small droplets. The steam in the

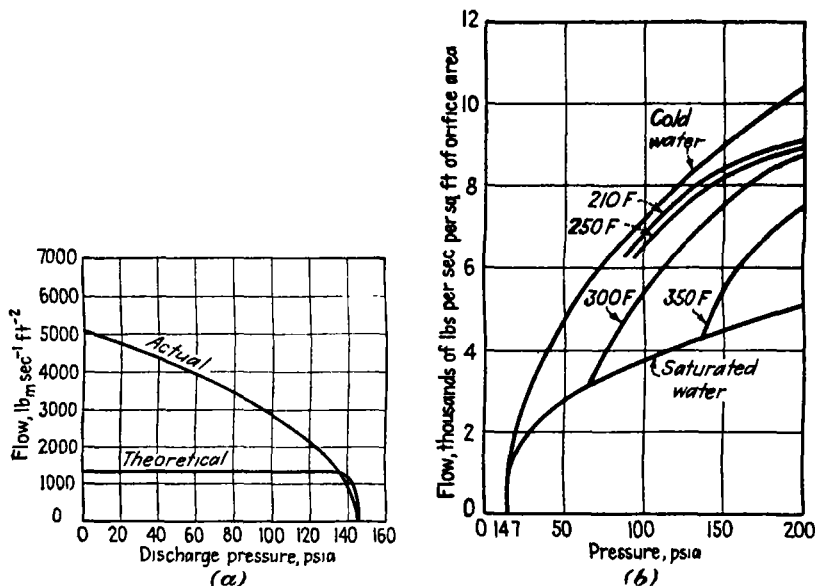


FIG 9-17 The mass flow rate of water through orifices (a) Saturated water and sharp-edged orifice with constant initial pressure of 145 psia (from reference 3) (b) Saturated and subcooled water and rounded entrance orifice (more closely, a flow nozzle) with constant discharge pressure of 14.7 psia (From D. R. Yarnall's discussion in reference 3)

interval between crossing the saturation line and condensing is in a metastable state and is said to be *supersaturated*. The same phenomenon occurs if saturated water is expanded through an orifice. It would be expected that the ebullition of vapor bubbles would occur as the water first entered the orifice because the pressure would be lower than the initial saturated pressure, but tests indicate that the phase change is delayed. Water, being relatively dense compared with the expected water-steam mixture, will allow a greater mass flow than the theoretical phase-equilibrium flow. This is illustrated by the test<sup>1</sup> results in Fig 9-17a, which show, too, the absence of a critical ratio for

<sup>1</sup> Reference 3

the actual sharp-edged orifice. If the orifice has a rounded approach, a change in phase may occur to some extent, but even here a much greater mass flow is experienced than would be expected from phase-equilibrium calculations (Fig. 9-17b).

Supersaturation of steam has been studied by several investigators.<sup>1</sup> In the normal course of events condensation of steam begins when the kinetic energy of the molecules is not sufficiently great to overcome the attractive forces between molecules; here and there throughout the gas, molecules are attracted to each other and group together to form a nucleus for further growth. As these molecular groups get larger, they become tiny droplets of condensate. Such a molecular process does not require a great amount of time, but expansion in a nozzle happens in an extremely small interval of time, and the temperature may be falling at a faster rate than the speed of agglomeration. When this delay in condensation occurs, the driving force for the molecular grouping is greatly increased because all through the gas will be molecules with insufficient energy to resist the molecular interattraction. Condensation begins at a rapid rate because, for the pressure experienced, the temperature is lower than that demanded for phase equilibrium.

The method<sup>2</sup> used by Yellott<sup>3</sup> is to expand steam through a nozzle that contains an axial tube with a ring of small radial holes communicating the pressure to a manometer. The tube can be shifted along the axis of the nozzle to measure the pressure at any stage of the expansion. The nozzle has glass sides to allow the flow to be observed by illumination from a beam of intense light passed axially along the nozzle. The entering steam is quite transparent; but, when condensation occurs, the light is scattered by the great number of small water droplets that form in the steam. Moving the axial search tube to this location allows the pressure at the start of condensation to be measured (see Fig. 9-3).

From his experiments on convergent-divergent nozzles, Yellott concluded that, for pressures up to 300 psia, the condensation pressure is below the critical pressure ratio computed for superheated steam, for this reason condensation occurs in the divergent section of the nozzle. Thus, supersaturation prevails beyond the throat of a nozzle, and the flow should be calculated on the basis of the metastable equilibrium instead of on the basis of thermal equilibrium between

<sup>1</sup> References 2, 4, 5, 6 and their bibliographies

<sup>2</sup> Reference 2

<sup>3</sup> References 4 and 5

vapor and liquid particles. To calculate the state of supersaturated steam, the perfect-gas equations can be extrapolated into the metastable region. In other words, although a phase boundary is crossed, condensation is delayed, and the empirical equations for superheated steam [Eqs (9-9a) and (9-10a)] and the perfect-gas equations [Eqs (9-5) and (9-23)] are closer approximations to the supersaturated state than the thermal-equilibrium equations (9-1) and (9-22). In effect, the flow of the metastable fluid from entrance to throat of the nozzle is a reversible expansion because delayed (and therefore irreversible) condensation does not occur until after the throat has been passed. Conceivably, the flow before condensation could be reversed and the initial state regained, thus, the metastable flow is a reversible<sup>1</sup> flow. For this reason the polytropic exponent in the perfect-gas equations, applied to the metastable state, will retain the value for an isentropic expansion of superheated steam.

The effect of supersaturation on the velocity and mass flow of steam will be considered in the following examples.

**Example 12.** Saturated steam at 50 psia flows through a round nozzle, with throat diameter of 1 in., to a discharge pressure of 30 psia. Calculate the ideal velocity and the ideal flow rate if velocity of approach is zero and phase equilibrium is assumed at each stage of the expansion.

**Solution.** If phase equilibrium is maintained, condensation will begin at the very start of the expansion, and the  $pv$  relationship will follow closely the empirical equation

$$pv^{1.13} = C \quad (9-9b)$$

The critical ratio is closely 0.58 [Eq (9-10b)], and the corresponding pressure is

$$p = 50(0.58) = 29 \text{ psia}$$

In this case the nozzle can be made convergent because the exit pressure of 30 psia is above the value for the critical ratio.

The thermal-equilibrium velocity can be found from Eq (9-3)

$$V_{\text{rev}} = \sqrt{2Jg_c(h_1 - h_2)_{\text{isen}}}$$

From the Steam Tables

At 50 psia	At 30 psia	
$s_1 = 1.6585 \text{ Btu lb}_m^{-1} \text{ F}^{-1}$	$s_f = 0.3680$	$s_{fg} = 1.3313$
$h_1 = 1174.1 \text{ Btu lb}_m^{-1}$	$v_g = 13.746$	$h_{fg} = 945.3$
$v_1 = 8.515 \text{ ft}^3 \text{ lb}_m^{-1}$		$h_f = 218.82$

<sup>1</sup> After the condensation, if the process were reversed, the same series of states could not be retraced, and the change of state into dry steam would occur at a temperature higher than the condensation temperature experienced in the expansion process.

Solving for quality at constant entropy,

$$\begin{aligned} s_f + x s_{fg} &= 1.6585 \\ x &= \frac{1.6585 - 0.3680}{1.3313} = 0.97 \\ v_2 &\approx 13.746(0.97) = 13.3 \text{ ft}^3/\text{lb}_m \\ h_2 &= 218.82 + 0.97(945.3) = 1134.8 \text{ Btu/lb}_m \end{aligned}$$

Substituting these values in Eq. (9-3) (and  $\sqrt{2g\phi J} = 223.77$ ),

$$V_{2 \text{ rev}} = 223.77 \sqrt{1174.1 - 1134.8} = 1,398 \text{ ft/sec}$$

The ideal mass flow for an expansion through a continuous series of equilibrium states is

$$\begin{aligned} m &= \frac{AV}{v} = \frac{(\pi/4)(1/144)1,398}{13.3} \\ &= 0.574 \text{ lb}_m/\text{sec} \quad \text{Ans} \end{aligned}$$

**Example 13:** Repeat Example 12, but assume the flow is supersaturated and that the perfect-gas equations will adequately portray the true conditions.

**Solution:** Equation (9-5b) will be used with  $pv$  substituted for  $RT$ .

$$V_{2 \text{ rev}} = \sqrt{\frac{2g_c k}{k-1} p_1 v_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]}$$

Substitute

$$p_1 = 50(144) \text{ lb}_f/\text{ft}^2 \quad v_1 = 8.515 \text{ ft}^3/\text{lb}_m \quad k = 1.31$$

(where  $k$  is found from Fig. 8, K & K Steam Tables)

$$\begin{aligned} V_{2 \text{ rev}} &= 8.02 \sqrt{\frac{1.31}{0.31} 7200(8.515) [1 - (0.6)^{0.237}]} \\ &= 1,372 \text{ ft/sec} \end{aligned}$$

Hence, the velocity attained in the supersaturated state is less than the velocity for phase-equilibrium expansion.

The specific volume of the gas at the throat is

$$\begin{aligned} v_2 &= v_1 \left( \frac{p_1}{p_2} \right)^{\frac{1}{k}} \\ &= 8.515(1.660)^{0.765} \\ &= 12.55 \text{ ft}^3/\text{lb} \end{aligned}$$

Note that the specific volume is less than that found in Example 12, therefore, the density is greater.

The mass flow is

$$\begin{aligned} m &= \frac{AV}{v} \\ &= \frac{(\pi/4)(1/144)1372}{12.55} \\ &= 0.597 \text{ lb}_m/\text{sec} \quad \text{Ans} \end{aligned}$$

The mass flow is greater than that found in Example 13. Note that in the actual test the value of  $0.597 \text{ lb}_m \text{ sec}^{-1}$  would be approached and not  $0.574 \text{ lb}_m \text{ sec}^{-1}$ , hence if the test had been based on the latter value as the ideal value, the discharge coefficient would approach

$$C = \frac{0.597}{0.574} = 1.04$$

Coefficients of discharge over 1.0, such as this, led to the study of supersaturation.

The temperature at the throat can be calculated from the polytropic relationship

$$\begin{aligned} \frac{T_2}{T_1} &= \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \\ T_2 &= 741(0.887) = 658 \text{ R or } 198 \text{ F} \end{aligned}$$

The phase-equilibrium temperature corresponding to the throat pressure of 30 psia can be found from the Steam Tables

$$t = 250 \text{ F}$$

Hence, the metastable undercooling is  $250 - 198 = 52 \text{ F}$

**Example 14.** Determine the area of the throat of a nozzle that will discharge  $1.0 \text{ lb}_m \text{ sec}^{-1}$  of steam if the coefficient of discharge is 0.98. The initial state of the steam is 50 psia, saturated, and discharge pressure is 30 psia. (Data are basically the same as in Examples 12 and 13.)

**Solution:** Since the coefficient of discharge is less than 1.0, it can be assumed, for want of better information, that the coefficient is based on supersaturated flow and not phase-equilibrium flow. The applicable equation for solution would be Eq. (9-23) multiplied by a discharge coefficient  $C$ . However, Example 13 has developed the necessary relations

$$m = C \frac{AV}{v}$$

Substituting the known values,

$$\begin{aligned} A &= \frac{mv}{CV} = \frac{1.0(12.55)}{0.98(1,372)} = 0.00935 \text{ ft}^2 \\ &= 1.345 \text{ in}^2 \quad \text{Ans} \end{aligned}$$

Assuming that the nozzle is round (although rectangular nozzles are not uncommon),

$$D = 1.31 \text{ in} \quad \text{Ans}$$

**Example 15:** Repeat Example 14 but assume that the nozzle efficiency is 0.95

**Solution:** By Eq. (9-14),

$$C_v = \sqrt{\eta_n} = \sqrt{0.95} = 0.975$$

The ideal velocity was found in Example 13

$$V_{2 \text{ rev}} = 1,372 \text{ ft/sec}$$

Hence,

$$V_{2 \text{ act}} = C_v V_{2 \text{ rev}} = 0.975(1,372) = 1,340 \text{ ft/sec}$$

Since the velocity is less than the ideal value because of friction, then the specific volume must have increased for the same reason. The specific volume could be easily found if the  $n$  value for the expansion were known. The  $n$  value can be calculated by Eq (9-4b), and some labor is avoided by noting that

$$V_2 = C_e F_c \sqrt{\frac{2g_c k p v}{k-1} \left[ 1 - r_p^{\frac{k-1}{k}} \right]} = F_c \sqrt{\frac{2g_c k p v}{k-1} \left[ 1 - r_p^{\frac{n-1}{n}} \right]}$$

which reduces to

$$r_n \left[ 1 - r_p^{\frac{k-1}{k}} \right] = \left[ 1 - r_p^{\frac{n-1}{n}} \right]$$

Since in most problems the radical on the left-hand side must be evaluated to find the ideal velocity, the extra labor in finding  $n$  by this method is small. By this means for the data of this problem

$$n = 1.283$$

and

$$\begin{aligned} p_1 v_1^n &= p_2 v_2^n \\ v_2 &= \left( \frac{p_1}{p_2} \right)^{\frac{1}{n}} v_1 = \left( \frac{50}{30} \right)^{0.78} 8.515 \\ v_2 &= 12.68 \text{ ft}^3/\text{lb}_m \end{aligned}$$

As before,

$$\begin{aligned} A &= \frac{mv}{V} = \frac{1.0(12.68)}{1340} = 0.00945 \text{ ft}^2 \\ &= 1.36 \text{ in}^2 \quad \text{Ans} \end{aligned}$$

And for a round nozzle

$$D = 1.315 \text{ in} \quad \text{Ans}$$

This method of solution, of course, is not restricted to supersaturated-expansion problems.

In Fig 9-18 is shown a Mollier chart locating the region of condensation for a flow of supersaturated steam. This region is called the *Wilson zone* and lies between the 2 and 4.5 per cent moisture line, condensation always starts in this zone, regardless of the initial pressure and temperature. If the nozzle is long, thus permitting a slow expansion, a *preliminary condensation* occurs at about the 2 per cent moisture line and slowly increases in amount. In the neighborhood of the 4 per cent moisture line the condensation is particularly violent whether or not a preliminary condensation was present; hence, this condition is called the *ultimate condensation*, and the locus of condensation points is called the *Wilson line*. For smooth short nozzles, only the ultimate condensation occurs. The ultimate condensation pressure apparently bears a fixed relation to the saturation pressure as illustrated in Fig 9-19.

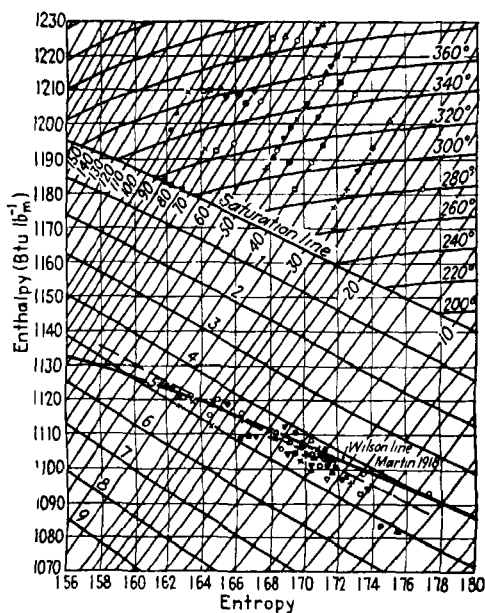


Fig 9-18 Mollier diagram showing region of ultimate condensation and experimental data (from reference 4)

It would be thought that further expansion in the two-phase region would be an equilibrium expansion between liquid and gas. However,

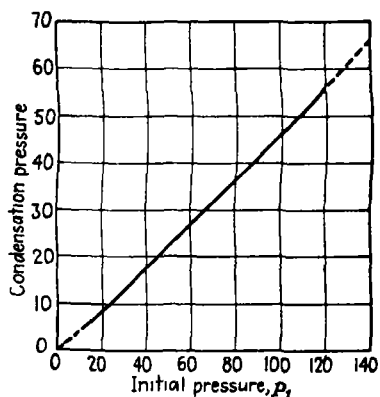


Fig 9-19 Condensation pressure as related to the initial pressure (steam initially saturated) (from reference 4).

since supersaturation is merely an event in a quick expansion, it can occur at any stage. For example, if the steam entering a nozzle is quite wet, it behaves as a mechanical mixture of saturated steam and drops of water. In expanding, the part of the mixture that is saturated steam undoubtedly becomes supersaturated as a step in the condensation process. However, a two-phase mixture of water and steam adds considerable difficulty to calculations or to experimental investigation. For example, the water particles will probably move

at a slower pace than the steam, and the temperatures of the two phases will probably differ. The problem of continuing supersaturation

throughout the two-phase region is obscured by the presence of the water phase and its effect upon the observed flow. Rational design of nozzles to allow for the effects of condensation cannot be made until more information is available upon these points.

That supersaturation is a loss can be realized by noting that for equilibrium expansion of steam and droplets in the two-phase region the value for  $k$  in the equation  $pv^k$  is about 1.13. If the flow is super-saturated, the value for  $k$  is about 1.31. The increase in kinetic energy for either process is equal to the  $-\int v dp$ , and the equation with the smaller exponent will give the greater value for this integral (Art. 8-9).

**9-18. Jet Pumps.** Ejectors are commonly used as vacuum pumps because of their low cost, simplicity, and dependability. The principle of the ejector depends upon the entrainment of a gas by a high-velocity fluid jet, the resulting mixture being compressed in a diffuser and discharged at a pressure higher than that in the gas chamber. Figure 9-20 is a diagrammatic sketch of a single-stage steam ejector that can be used to produce a vacuum of 26 in. of mercury. Steam enters the ejector at high pressure and expands in a convergent-divergent nozzle. The high-velocity fluid leaving the nozzle passes through the air chamber and entrains part of the air to be evacuated. The mixture of air and fluid then enters a convergent-divergent diffuser that recompresses the mixture to the discharge pressure. The convergent-divergent diffuser is necessary because in normal operation the pressure in the air chamber will be low and the velocity of the steam jet will be supersonic. To recompress such a stream the diffuser must first converge and then diverge as the velocity falls below the acoustic

For creating a low vacuum or discharging to a higher back pressure, several ejectors can be connected in series and called, respectively, first, second, etc., stages with the last stage discharging directly or indirectly into the atmosphere. A small condenser called the *inter-condenser* can be used between stages to condense the steam of each stage, thus relieving subsequent stages that need only compress those

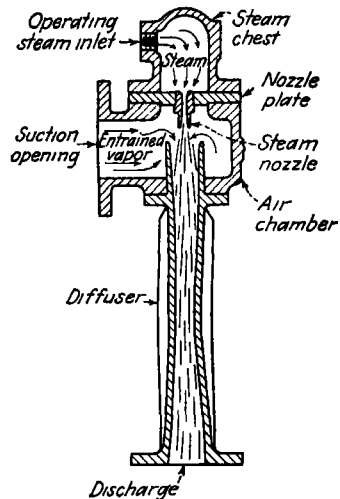


FIG. 9-20 Steam ejector (Elliott Co.)



gases that are noncondensable In Fig 9-21 is illustrated a two-stage ejector with inter- and aftercondensers This type can be used for evacuating steam condensers and will maintain an absolute pressure of 1 in. of mercury

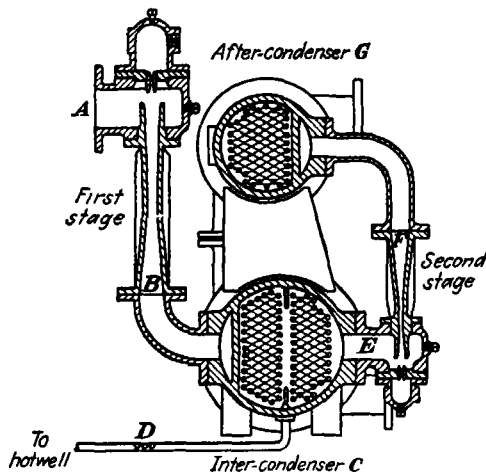


FIG 9-21 Two-stage air ejector (Elliot Co)

Assume that this pump is attached to a steam condenser similar to that shown in Fig 3-22 The steam-air mixture at a pressure of, closely, 1 in mercury is withdrawn from the condenser at A This

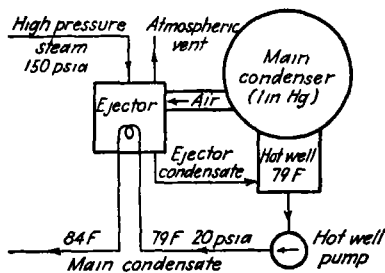


FIG 9-22 Ejector flow circuit in power plant

mixture is entrained and compressed to a pressure of about 7 in mercury in the first stage (B) and discharged into the intercondenser (C) where cooling and condensation take place The condensed steam is drained back into the main condenser through a suitable resistance (D) (necessary because of the difference in pressures), while the air saturated with steam (E) passes to the second stage

A similar action takes place in this stage with discharge (F) to a pressure slightly above atmospheric pressure within the aftercondenser (G). Here the noncondensable gases are vented to the atmosphere.

It is of interest to note that the condensers of the ejector can and usually do serve as feed-water heaters for the main condenser con-

densate by using the condensate as the coolant (Fig 9-22). In this manner the steam used to actuate the ejector serves two useful purposes

Three-stage ejectors are used where the absolute pressure must be maintained between 0.1 and 1 in. of mercury while four stages are necessary for pressures between 0.01 and 0.1 in. of mercury

A jet pump used to pump water is called an *injector*. In Fig 9-23 steam from the boiler passes to the injector and expands in the nozzle to a low pressure while acquiring a high velocity. Water is drawn into the chamber around the nozzle and accelerated in the combining tube by the steam jet, which is itself condensed. The mixture of water and steam is compressed in the delivery tube while being slowed down, and a pressure is finally achieved that can be greater than the boiler

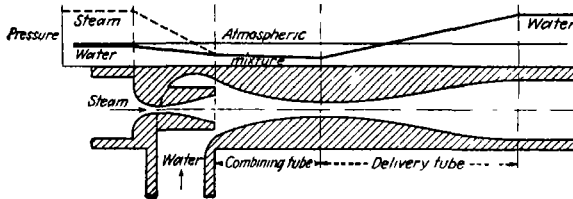


FIG 9-23 Injector

pressure. At first glance such action may seem improbable, but note that the expansion of the steam transforms available energy of amount  $-\int v dp$  for a vapor into kinetic energy. This kinetic energy is used to lift and accelerate a water column, and the action is most inefficiently done because the process is highly irreversible. But the kinetic energy necessary for the compression of the liquid ( $-\int v dp$  for the condensed steam and pumped water) back to the initial pressure is but a small fraction of the energy that was available, and no trouble is experienced in achieving pressures much higher than the initial pressure. This is but another example of Art. 3-6b, the work that must be done to compress a vapor, or that is realized from expanding a vapor, is much greater than the work required to compress a liquid.

Upon starting the injector, condensation of the steam will not occur until water enters the combining tube and the discharge escapes through an overflow pipe (not illustrated). After condensation begins, the pressure will build up and delivery can be made to the boiler. If hot water is led to the injector, vaporization of the water occurs as the pressure is decreased, and satisfactory operation is difficult to achieve.

It should be realized that mixing hot and cold fluids results in a loss in availability (Art. 5-11). A boiler installation not using feed-

water heaters must pump cold water into the boiler. An injector combines in part this irreversible operation with the pumping, but the inefficiency of the injector is no greater loss than the inefficiency of the mixing process. For this reason injectors are used where cold water is pumped into steam boilers such as the locomotive boiler. The efficiency of the injector as a pump is of the order of 1 per cent, but this is immaterial because the water is introduced into the boiler without supplying work from an external source. However, in modern plants, to reduce the loss in availability that is caused by mixing hot and cold fluids, the feed water is passed through numerous feed-water heaters before the water enters the boiler. Since the injector needs cold water for best operation, in most plants it is more convenient to use centrifugal pumps.

### 9-19. Nonsteady-flow Problems.<sup>1</sup> a

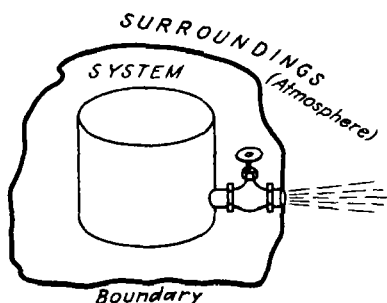


FIG 9-24 Adiabatic flow into surroundings of infinite extent

A frequently encountered flow process is the adiabatic emptying of a tank (the system) that is connected to surroundings of unchanging properties. In many cases the atmosphere is the invariant surroundings. For example, in Fig 9-24 a free expansion of fluid occurs through the valve to the atmosphere, and the properties and mass of the fluid in the system are continually changing. The problem is to analyze this nonsteady-

flow process. For this system the decrease in energy is equal to the change in internal energy<sup>2</sup>

$$\Delta E = \Delta U = m_2 u_2 - m_1 u_1 \quad (9-31)$$

Now let attention be directed to the part of the fluid that escapes from the system. Suppose the valve acts as a perfect nozzle, then, the temperature of the fluid leaving the nozzle will be constant during the

<sup>1</sup> This subject was briefly introduced in Art 2-10

<sup>2</sup> Equation (9-31) cannot be evaluated unless the absolute values of internal energy are known. Consider steam to be the fluid, values of internal energy ( $u'$ ) selected from a Steam Table are evaluated above an arbitrary datum, say, 32 F.

$$\begin{aligned} \Delta U &= m_2(u_2' + u_{32 \text{ F}}) - m_1(u_1' + u_{32 \text{ F}}) \\ &= m_2 u_2' - m_1 u_1' + (m_2 - m_1) u_{32 \text{ F}} \end{aligned}$$

and  $(m_2 - m_1) u_{32 \text{ F}}$  cannot be evaluated because  $u_{32 \text{ F}}$  is unknown

entire reversible process The first element of fluid will expand from the initial temperature and pressure and will acquire a high velocity and low temperature Succeeding elements will expand from lower pressures and temperatures to the same constant surrounding pressure and will acquire the same temperature<sup>1</sup> as the first element but decreasing velocities An observer evaluating the energy leaving the system would recognize internal, flow, and kinetic energy in the flowing mass:

$$\begin{aligned} E_{\text{flow}} &= \sum m \left( u_f + p_f v_f + \frac{1}{2g_c} V_f^2 \right) \\ &= \int_0^{m_1 - m_2} h_f dm + \int_0^{m_1 - m_2} \frac{V_f^2}{2g_c} dm \end{aligned}$$

where  $f$  = instantaneous state of the fluid in the stream

This equation can be simplified by noting that during the reversible expansion the temperature and pressure of the leaving stream is constant, and therefore the enthalpy is constant (although kinetic energy is of ever-changing value)

$$E_{\text{flow}} = [(m_1 - m_2)h_f + \text{KE}_{\text{rev}}]_{s=c} \quad (9-32)$$

Here the summation of the variable kinetic energy is shown by the symbol  $\text{KE}_{\text{rev}}$  The decrease in energy indicated by Eq (9-31) must equal the energy of flow indicated by Eq (9-32) (but of opposite sign):

$$\begin{aligned} (m_1 - m_2)h_f + \text{KE}_{\text{rev}} &= m_1 u_1 - m_2 u_2 \\ \text{KE}_{\text{rev}} &= [m_1 u_1 - m_2 u_2 - (m_1 - m_2)h_f]_{s=c} \end{aligned} \quad (9-33a)$$

where subscripts 1 = initial state of the fluid in the tank (system)

2 = final state of the fluid in the tank (system)

$f$  = state of fluid in flow

If the pressure in the tank is reduced to atmospheric, Eq (9-33a) becomes

$$\text{KE}_{\text{rev}} = [m_1 u_1 - m_2 u_f - (m_1 - m_2)h_f]_{s=c} \quad (9-33b)$$

The kinetic energy obtained in this expansion could be converted into work by a perfect turbine without changing the properties of internal energy and enthalpy, therefore,

$$W_{\text{rev}} = \text{KE}_{\text{rev}} = [m_1 u_1 - m_2 u_f - (m_1 - m_2)h_f]_{s=c} \quad (9-33c)$$

<sup>1</sup> However, if a thermometer with unity recovery factor is placed in front of the stream of discharged fluid, the impact temperature will steadily decrease since it will always be equal to the instantaneous temperature of the fluid in the tank Similarly, if the valve is replaced by a porous plug, the temperature of the fluid irreversibly leaving the system will progressively decrease

[Equation (9-33) could also have been obtained from the general First Law equation (3-4) ]

Other relationships can be derived from the perfect-gas equations for the nonsteady discharge process. The temperature of the fluid in the tank at any instant equals

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \quad (8-11)$$

since the process of rapid expansion is essentially adiabatic and reversible. The mass of fluid in the tank at any instant is found by the equation of state

$$\frac{m_2}{m_1} = \frac{p_2 V / RT_2}{p_1 V / RT_1} = \frac{p_2 T_1}{p_1 T_2} = \left( \frac{p_2}{p_1} \right)^{\frac{1}{k}} = \frac{v_1}{v_2} \quad (9-34)$$

Equation (9-33c) can also be derived by devising a reversible closed system that will be equivalent to the reversible open system. Consider the system to be the entire mass of fluid  $m_1$  but contained in a cylinder and piston. Let the fluid expand from the initial to the final state and move the piston that is connected to an external load, the piston must also do work in pushing back the atmosphere. By the First Law

$$Q - W = \Delta U$$

And for an adiabatic expansion

$$W = m_1(u_1 - u_f)$$

But the net work is less than  $W$  by an amount equivalent to the energy expended in pushing aside the atmosphere

$$W_{\text{net}} = m_1(u_1 - u_f) - p_f(V_2 - V_1) \quad (9-35a)$$

$$W_{\text{net}} = m_1[(u_1 - u_f) - p_f(v_f - v_1)] \quad (9-35b)$$

The net work evaluated by Eqs (9-35) (when restricted to isentropic expansion) is equal to the net work, the kinetic energy, evaluated by Eq (9-33c)

**Example 16:** A tank with volume of 50 cu ft is filled with air at a pressure of 100 psia and a temperature of 240 F. If this air is used to drive a turbine, what will be the maximum amount of work that can be obtained by adiabatic expansion to atmospheric pressure? (Atmospheric conditions,  $p = 14.7$  psi and  $t = 60$  F)

**Solution:** The maximum amount of work will be received if the adiabatic expansion is reversible and all the kinetic energy is transformed into work by the turbine, Eq (9-33c) or (9-35) evaluates this limiting amount of work. Since the

final temperature of the air in the tank is the same temperature as that of the high-velocity stream,

$$\frac{T_1}{T_f} = \frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}} = \left(\frac{100}{14.7}\right)^{0.286} = 1.954$$

$$T_f = T_2 = 358 \text{ R}$$

and

$$m_1 = \frac{p_1 V}{RT_1} = \frac{100(50)}{(10.73/29)700} = 19.3 \text{ lb}_m$$

$$m_2 = \frac{p_2 V}{RT_2} = \frac{14.7(50)}{(10.73/29)358} = 5.55 \text{ lb}_m$$

By Eq (9-33c)

$$W_{\text{rev}} = m_1 u_1 - m_2 u_f - (m_1 - m_2) h_f \quad (9-33c)$$

and for perfect gases

$$\begin{aligned} W_{\text{rev}} &= c_v(m_1 T_1 - m_2 T_f) - (m_1 - m_2) c_p T_f \\ &= 0.171[19.3(700) - 5.55(358)] - (19.3 - 5.55)(0.24)(358) \\ &= 790 \text{ Btu} \quad \text{Ans} \end{aligned}$$

This answer can be checked by Eq (9-35a)

$$\begin{aligned} W_{\text{rev}} &= [m_1(u_1 - u_f) - p_f(V_2 - V_1)]_{s=c} \\ &= m_1 c_v(T_1 - T_f) - p_f \left( \frac{m_1 R T_2}{p_2} - \frac{m_1 R T_1}{p_1} \right) \\ &= m_1 c_v(T_1 - T_2) - m_1 R \left( T_2 - \frac{p_2}{p_1} T_1 \right) \\ &= 19.3(0.171)(700 - 358) - 19.3 \left( \frac{1.986}{29} \right) \left( 358 - \frac{14.7}{100} 700 \right) \\ &= 790 \text{ Btu} \quad \text{Ans} \end{aligned}$$

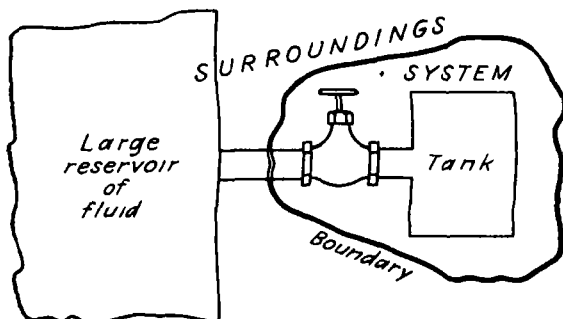


FIG 9-25 Adiabatic flow from surroundings of infinite extent.

*b* Consider next the inverse process of adiabatically filling a tank from an infinite reservoir as illustrated in Fig 9-25. Equation (3-5) can be applied to this process

$$Q - W = - \sum m_f \left( u_f + p_f v_f + \frac{V_f^2}{2g_c} \right)_{\text{flow in}} + (m_2 u_2 - m_1 u_1)_{\text{storage}}$$

where  $Q, W = 0$ , and  $V_f$  will approach zero by locating the boundary of the system some distance from the valve. Since  $T_f$  and  $p_f$  are constant,  $h_f$  is constant:

$$\sum m_f h_f = \int_0^{m_2 - m_1} h_f dm_f = (m_2 - m_1) h_f$$

$$(m_2 - m_1) h_f = m_2 u_2 - m_1 u_1 \quad (9-36a)$$

For perfect gases

$$(m_2 - m_1) c_p T_f = c_v (m_2 T_2 - m_1 T_1) \quad (9-36b)$$

The use for these equations will be illustrated by an example

**Example 17:** A small evacuated container is connected to a large steam line that contains saturated steam at a pressure of 100 psia. If the container is filled with steam to the line pressure, what will be the final state of the steam? (Assume both heat capacity of container and heat losses to be zero.)

**Solution:** Equation (9-36a) is applicable

$$(m_2 - m_1) h_f = m_2 u_2 - m_1 u_1$$

but, since the container is initially evacuated,

$$m_1 = 0$$

$$u_1 = 0$$

and

$$m_2 h_f = m_2 u_2$$

or

$$u_2 = h_f$$

From the Steam Tables, for 100 psia saturated steam,

$$h_f = 1187.2 \text{ Btu/lb}_m \quad t = 328 \text{ F}$$

The final conditions are

$$p_2 = 100 \text{ psia}$$

$$u_2 = h_f = 1187.2 \text{ Btu/lb}_m$$

Interpolating in Steam Table 3 for these values,

$$t_2 \approx 540 \text{ F} \quad \text{Ans}$$

$$p_2 = 100 \text{ psia}$$

And the temperature rise from compression of the steam in the container is

$$540 - 328 = 212 \text{ F} \quad \text{Ans}$$

Note that Eq (9-36a) can be written

$$(m_2 - m_1)(u'_f + u_{32 \text{ F}} + pv) = m_2(u'_2 + u_{32 \text{ F}}) - m_1(u'_1 + u_{32 \text{ F}})$$

where  $u_{32 \text{ F}}$  is the internal energy at the datum state of the Steam Tables

Then,

$$(m_2 - m_1)h_f' + (m_2 - m_1)u_{22F} = m_2u_2' - m_1u_1' + (m_2 - m_1)u_{22F}$$

or

$$(m_2 - m_1)h_f' = m_2u_2' - m_1u_1'$$

and here the datum value for internal energy can be canceled

### Problems

1. Steam expands from an initial state of  $p = 500$  psia,  $t = 700$  F, to 300 psia. Determine the velocity attained by an adiabatic and reversible expansion if the velocity of approach is zero.
2. Repeat Prob 1, assuming that the velocity of approach is 300 ft sec<sup>-1</sup>. What is the value of  $\beta$  for this problem?
3. Determine for the conditions of Prob 1 the highest approach velocity that can be neglected if the calculated final velocity is to be within 2 per cent of the true answer.
4. Air expands from 100 psia and 400 F to atmospheric pressure. Determine the velocity attained after an adiabatic and reversible expansion from a region of infinite extent.
5. If in Prob 4 only 95 per cent of the theoretical velocity is realized at any stage of the expansion, what should be the value of  $n$  assigned to this irreversible process?
6. Repeat Prob 1, assuming that the exhaust pressure is 150 psia.
7. Determine the variation in area throughout the nozzle of Prob 4 for a mass flow of 1 lb<sub>m</sub> sec<sup>-1</sup>.
8. Determine the variation in area throughout the nozzle of Prob 6 for a mass flow of 1 lb<sub>m</sub> sec<sup>-1</sup>.
9. Determine the critical pressure ratios for Probs 4 and 6 and check by the data of Probs 7 and 8.
10. A perfect nozzle is to expand carbon dioxide adiabatically from 500 psia and 300 F to 25 psia. Determine the area and diameter at the throat that will allow an ideal mass flow rate of 0.25 lb<sub>m</sub> sec<sup>-1</sup>. (Consider carbon dioxide to behave as a perfect gas.)
11. Repeat Prob 10, using  $T$ 's diagram in Appendix (Fig. III).
12. A perfect nozzle is to expand air adiabatically from a pressure of 50 atm and 400 R to 5 atm. Determine the area and diameter at the throat that will allow an ideal mass flow rate of 0.25 lb<sub>m</sub> sec<sup>-1</sup>. (Consider air to behave as a perfect gas.)
13. Repeat Prob 12, but use the  $T$ 's diagram (Fig. II, Appendix) and compressibility data (Fig. VII, Appendix).
14. Show all steps in derivation of Eqs (9-7) and (9-8).
15. A perfect nozzle has an adiabatic mass flow rate of 2 lb<sub>m</sub> sec<sup>-1</sup> of nitrogen from a pressure of 100 psia and temperature of 300 F to 10 psia. Determine the throat and exit area of the nozzle.
16. Repeat Prob 15, assuming  $\beta = 0.80$ .
17. Derive an expression for the mass flow rate through an ideal nozzle wherein the critical pressure ratio exists, and show that the expression is equivalent to

$$m = (\text{constant}) A_1 p_1 / \sqrt{T_1}$$



18. Determine the Mach numbers for the sections selected in Prob 7
19. From the data of Probs 4 and 5 determine the nozzle efficiency, velocity coefficient, specific volume at exit and throat, and probable discharge coefficient. Calculate the discharge coefficient for both the throat and exit areas and compare values. Discuss
20. If the efficiency of the nozzle in Prob 6 is 0.95, determine the velocity, specific volume, and probable discharge coefficient
21. Assume that the velocity coefficient from entrance to throat of the nozzle of Prob 15 is 0.98 while the over-all value is 0.96. (a) Determine the velocity and specific volume at throat and exit. (b) Determine new throat and exit areas
22. For the data of Probs 15 and 16 assume that the real nozzle can be assigned a value of  $n = 1.35$ . Determine the throat and exit areas and the pressure at the throat
23. For the data of Prob 10, determine the dimension of the throat of a real nozzle that has a discharge coefficient of 0.95
24. Repeat Prob 23 but for the data of Prob 12
25. Air is flowing through an 8-in. pipe and through a 2-in. thin plate orifice. The "adiabatic" coefficient of discharge is 0.65, and the differential manometer reading is 30 in. water. The upstream temperature of the air is 80 F, and upstream pressure is 10 psig. Compute the flow rate
26. Derive Eqs (9-23), (9-24), and (9-25)
27. Repeat Prob 25, assuming that the pipe is 4 in. in diameter and the pressure drop across the orifice is 30 in. Hg
28. A 4-by-2-in. venturi has a coefficient of discharge of 0.98. Air is flowing to the venturi under a pressure of 50 psig and temperature of 60 F. The pressure drop to the throat of the venturi is 12 in. water. Determine the mass flow rate
29. A 1-in. (diameter) flow nozzle is installed in a 2-in. pipe that carries air at 12 in. water gauge pressure. The temperature of the air is 60 F, the discharge coefficient for the nozzle is 0.97, and the pressure drop across the nozzle is 6 in. water. Compute the mass flow rate
30. Derive Eq (9-28)
31. Air is flowing through a 6-in. pipe and is metered by a 1.5-in. thin plate orifice with flange taps. The upstream conditions are  $p = 20$  psig,  $t = 100$  F. The manometer drop across the orifice is 30 in. Hg. Determine the mass flow rate (ASME procedure)
32. Repeat Prob 31 if water is the fluid flowing and the pressure difference across the orifice is 30 in. Hg
33. Repeat Prob 31 if the fluid is carbon dioxide. Use compressibility data
34. For the data of Prob 4 determine the temperature that would be indicated by a thermal meter with recovery factor of 0.8 if it were to be inserted in the high-velocity stream at the mouth of the nozzle
35. Air is flowing through a 4-in. pipe under a static pressure of 3 in. water. A thermometer with recovery factor of 1.0 indicates a temperature of 100 F while the mean velocity head calculated from pitot-tube readings is 2.08 in. water. Determine the average velocity of the air and the mass flow rate. (Barometer shows 29.90 in. Hg)
36. Repeat Prob 35, assuming that the mean impact pressure calculated from the pitot-tube readings is 3.5 in. water
37. Repeat Prob 35, assuming that the static pressure is 10.25 psig and the pitot-tube calculations show a mean impact pressure of 30.06 psia

**38.** Saturated steam at 100 psia flows through a nozzle to a discharge pressure of 40 psia. For a mass flow rate of  $1 \text{ lb}_m \text{ sec}^{-1}$  determine the area, velocity, and specific volume at 100, 80, 60, 55, and 50 psia. Assume phase equilibrium throughout the reversible and adiabatic expansion.

**39.** (a) Repeat Prob 38, assuming that the flow is supersaturated, and compare answers. (b) Determine the undercooling and pressure ratio at the throat.

**40.** Repeat Prob 39, assuming the coefficient of discharge to be 0.97.

**41.** Saturated steam flows through a nozzle with throat area of  $0.25 \text{ in}^2$  from a large system wherein  $p_1 = 200 \text{ psia}$  to a region where  $p = 20 \text{ psia}$ . Calculate the mass flow rate if the discharge coefficient is 0.98.

**42.** Superheated steam at 100 psia and 360 F passes through a nozzle to a discharge pressure of 40 psia. If the area of the throat is  $0.50 \text{ in}^2$  and the coefficient of discharge is 0.98, calculate the mass flow rate.

**43.** Superheated steam at 400 psia and 500 F expands through a nozzle to a discharge region at 150 psia. Calculate the dimensions of a nozzle that will pass  $0.50 \text{ lb}_m \text{ sec}^{-1}$  if the discharge coefficient is 0.97.

**44.** In the same manner followed in deriving Eq (9-35), derive an equation for the case where  $p_2$  is not atmospheric and show that it is not equivalent to Eq (9-33a).

**45.** A tank contains  $20 \text{ lb}_m$  of air at a pressure of 100 psia and temperature of 400 F. A valve is opened, and a portion of the air quickly escapes while the pressure drops to 80 psia. How much air remains in the tank?

**46.** Repeat Prob 45, assuming that steam is the fluid and using the Steam Tables.

**47.** An insulated tank contains  $100 \text{ lb}_m$  of saturated steam at 20 psia. The tank is connected to a reservoir of saturated steam that is at 200 psia, and the tank is filled to reservoir pressure. (a) Set up the equations for an energy balance and a volume balance. (b) Estimate the final conditions of the steam by selecting a few trial values for internal energy and specific volume from the Steam Tables.

**48.** A tank filled with air at a pressure of 50 psia and temperature of 100 F is to be used to drive a turbine that is coupled to a small generator. The system is to be used for emergency power for a radio transmitter that requires 5 watts, and service for 10 min is desired. Assuming that the efficiency of using the air is 50 per cent, what should be the approximate size of the tank?

**49.** A patent for automotive engines proposes to hold the intake valve closed until a vacuum has been pulled in the cylinder and then to open the valve with consequent filling of the cylinder to atmospheric pressure. Assume that  $0.02 \text{ lb}_m$  of air is in the cylinder at a pressure of 4 psia and temperature of 20 F when the valve is opened. Calculate the final temperature of the air if heat losses are neglected. The outside air temperature is 25 F.

### Symbols and Units

<i>A</i>	area ( $\text{ft}^2$ )
<i>C</i>	discharge coefficient, also, a constant
<i>C<sub>v</sub></i>	velocity coefficient
<i>c</i>	heat capacity ( $\text{Btu lb}_m^{-1} \text{ R}^{-1}$ )
<i>D</i>	diameter (ft and in)
<i>E</i>	energy in general (Btu)

<b>F</b>	Fahrenheit temperature scale
$F_c$	correction factor for velocity of approach
$G$	specific gravity
$g$	local acceleration of gravity
$g_0$	standard acceleration of gravity ( $32.17 \text{ ft sec}^{-2}$ )
$g_c$	dimensional constant $\left(32.17 \frac{\text{lb}_m \text{ ft}}{\text{lb}_f \text{ sec}^2}\right)$
<b>H</b>	head (ft)
$h$	specific enthalpy ( $\text{Btu lb}_m^{-1}$ )
$J$	Joule's equivalent ( $778.16 \text{ ft lb}_f \text{ Btu}^{-1}$ )
<b>KE</b>	kinetic energy ( $\text{ft lb}_f \text{ lb}_m^{-1}$ )
$K$	ASME discharge and approach factor
$k$	isentropic exponent
$M$	molecular weight
$m$	mass, also, mass flow rate ( $\text{lb}_m$ and $\text{lb}_m \text{ sec}^{-1}$ )
$n$	polytropic exponent
$p$	pressure ( $\text{psi}$ and $\text{lb}_f \text{ ft}^{-2}$ )
$Q$	heat ( $\text{Btu}$ and $\text{Btu lb}_m^{-1}$ )
$R$	specific gas constant $\left(\frac{1,545 \text{ ft lb}_f}{M \text{ lb}_m \text{ R}}\right)$ or $\left(\frac{1,986 \text{ Btu}}{M \text{ lb}_m \text{ R}}\right)$
<b>R</b>	Rankine temperature scale
$r, R$	radius
$r_p$	pressure ratio
$r_{pt}$	minimum throat pressure ratio (critical pressure ratio)
$s$	specific entropy ( $\text{Btu lb}_m^{-1} \text{ R}^{-1}$ )
$t$	thermodynamic temperature
$T$	absolute thermodynamic temperature
$u$	specific internal energy ( $\text{Btu lb}_m^{-1}$ )
$U$	internal energy ( $\text{Btu}$ )
$v$	specific volume ( $\text{ft}^3 \text{ lb}_m^{-1}$ )
$V$	velocity ( $\text{ft sec}^{-1}$ ), also, volume ( $\text{ft}^3$ )
$W$	work
$x$	quality
$Y_1$	empirical ASME expansion factor for orifices
$z$	height (ft and in)

#### Subscripts and Abbreviations

$a$	acoustic
$f$	force, also, flow stream, also, saturated liquid
$g$	saturated vapor
$fg$	change from saturated liquid to saturated vapor
$m$	manometer, also, mass
$p$	pressure
$pt$	throat pressure
$t$	throat
$o$	impact values
<b>adia</b>	adiabatic
<b>avg</b>	average
<b>hyd</b>	hydraulic

irrev	irreversible
isen	isentropic
$Ma$	Mach number
max	maximum
psia	absolute pressure ( $\text{lb}_f/\text{in}^2$ )
psig	gauge pressure ( $\text{lb}_f/\text{in}^2$ )
$Re$	Reynolds number
rev	reversible

## Greek Letters

$\beta$	(beta)	diameter ratio of throat to approach section
$\gamma$	(gamma)	specific weight
$\rho$	(rho)	density
$\mu$	(mu)	viscosity
$\lambda$	(lambda)	recovery factor (temperature)
$\eta_n$	(eta)	nozzle efficiency
$\phi$	(phi)	ASME expansion factor for flow nozzles

## Suggested References

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## CHAPTER X

### MIXTURES OF GASES AND VAPORS

Gases may be mixed in any proportions to form an infinite number of different mixtures. Each mixture of gases could be treated as a single substance, and an equation of state could be determined, but the experimental work necessary to chart the behavior of all possible mixtures would be prohibitive. Thus, it becomes necessary to find methods of transforming data for the individual gas to account for the behavior of a mixture of gases.

#### 10-1. General Relationships between Mass and Mole Units.<sup>1</sup>

Consider a mixture made up of components *a*, *b*, and *c*. The mass of mixture must equal the sum of the masses of the components.

$$m = m_a + m_b + m_c \quad (10-1)$$

The composition of a mixture is best evaluated if the mole is used as the mass unit. The total number of moles in the mixture is defined as

$$n = n_a + n_b + n_c \quad (10-2)$$

The *mole fraction* *x* of fluids *a*, *b*, or *c* is defined

$$x_a = \frac{n_a}{n_a + n_b + n_c} \quad x_b = \frac{n_b}{n_a + n_b + n_c} \quad x_c = \frac{n_c}{n_a + n_b + n_c} \quad (10-3)$$

and, therefore,

$$x_a + x_b + x_c = 1.0 \quad (10-4)$$

The mole and the mass are related units defined by

$$m = nM \quad \text{and} \quad n = \frac{m}{M} \quad (7-6)$$

where *M* is the molecular weight. Equation (7-6) can be substituted in Eq. (10-1)

$$nM = n_a M_a + n_b M_b + n_c M_c = m \quad (a)$$

and the *average molecular weight* of the mixture is determined

$$M = x_a M_a + x_b M_b + x_c M_c \quad (10-5)$$

<sup>1</sup> It will be especially helpful in studying this chapter if the student will write out, in words, the meaning of each equation.



It should be recalled (Art 7-5) that the mole unit allows a *universal* gas constant  $R_0$  to be used for all gases while the pound or gram units of mass demand a *specific* gas constant that has different values for different gases. Hence, if a mass unit other than the mole is to be used for the mixture, a specific gas constant must be determined. The specific gas constant can be found from the relationship between the molecular weight and the universal gas constant.

$$R = \frac{R_0}{M} \quad (7-4)$$

Equation (7-4) can be used for either mixture or component

**10-2. Mixtures of Perfect Gases.** In a mixture of perfect gases, it can be conceived that each component will occupy the entire volume and display the common temperature while exerting only a fraction of the entire pressure. With this concept in mind, the equation of state for perfect gases can be substituted in Eq (10-2)

$$\begin{aligned} n &= n_a + n_b + n_c \\ \frac{pV}{R_0T} &= \frac{p_a V_a}{R_0 T_a} + \frac{p_b V_b}{R_0 T_b} + \frac{p_c V_c}{R_0 T_c} \end{aligned}$$

But

$$V = V_a = V_b = V_c \quad T = T_a = T_b = T_c$$

and therefore

$$p = p_a + p_b + p_c \Big]_{T, V}^* \quad (10-6)$$

Thus, by inverse reasoning to that of Art 7-2, *Dalton's law of partial pressures* is obtained

**The pressure of a mixture of perfect gases is equal to the sum of the partial pressures which the component gases would exert if each existed alone in the mixture volume at the mixture temperature.**

For the conditions of Dalton's law applied to the mixture and to one of the components,

$$\frac{p_i V_i}{p V} = \frac{n_i R_0 T_i}{n R_0 T}$$

and here

$$V_i = V \quad T_i = T$$

\* These subscripts indicate that the pressures are to be evaluated at the temperature and volume of the mixture

Hence,

$$\left. \frac{p_i}{p} \right]_{p,T} = \frac{n_i}{n} = x_i, \quad p_i = x_i p \Big]_{p,T} \quad (10-7)$$

Equation (10-7) shows that the partial pressure and the mole fraction of the component are proportional.

A slightly different and more imaginary concept can be applied to the mixture of gases. Suppose the mixture to be divided by imaginary partitions into spaces each occupied by a separate component. Each component, then, would exert the mixture pressure and temperature while occupying only a *partial volume* of the mixture. With this concept in mind, the perfect-gas equation can be again substituted in Eq (10-2)

$$\begin{aligned} n &= n_a + n_b + n_c \\ \frac{pV}{R_0 T} &= \frac{p_a V_a}{R_0 T_a} + \frac{p_b V_b}{R_0 T_b} + \frac{p_c V_c}{R_0 T_c} \end{aligned}$$

But here

$$p = p_a = p_b = p_c \quad T = T_a = T_b = T_c$$

and therefore

$$V = V_a + V_b + V_c \Big]_{p,T} \quad (10-8)$$

Equation (10-8) is called *Amagat's law* and, also, *Leduc's law*:

**The volume of a mixture of perfect gases is equal to the sum of the partial volumes which the component gases would occupy if each existed alone at the pressure and temperature of the mixture.**

The partial volume, like the partial pressure, is related to the mole fraction:

$$\frac{p_i V_i}{pV} = \frac{n_i R_0 T_i}{n R_0 T}$$

and here

$$p = p_i \quad T = T_i$$

Hence,

$$\left. \frac{V_i}{V} \right]_{p,T} = \frac{n_i}{n} = x_i, \quad V_i = x_i V \Big]_{p,T} \quad (10-9)$$

It is evident by Eq (10-9) that mixture and components have identical *specific* volumes

**Example 1:** A mixture of 10 lb<sub>m</sub> of oxygen and 15 lb<sub>m</sub> of nitrogen has a pressure of 50 psia and a temperature of 60 F. Determine for the mixture (a) the mole

\* All volumes are measured at the pressure and temperature of the mixture

fraction of each component, (b) the average molecular weight, (c) the specific gas constant, (d) the volume and density, (e) the partial pressures and partial volumes.

**Solution:** *a* The molecular weights of the components are found in Table VI (Appendix)

$$M_O = 32.00 \quad M_N = 28.02$$

The moles of mixture are

$$n_O = \frac{10 \text{ lb}_m}{32} = 0.3125 \text{ mole}$$

$$n_N = \frac{15 \text{ lb}_m}{28.02} = 0.5350 \text{ mole}$$

$$n = 0.8475 \text{ mole}$$

The mole fractions are

$$x_O = \frac{0.3125}{0.8475} = 0.369 \quad \text{Ans}$$

$$x_N = \frac{0.5350}{0.8475} = \frac{0.631}{1.000} \quad \text{Ans}$$

*b* The average molecular weight is obtained from Eq (10-5)

$$M = x_O M_O + x_N M_N$$

$$M = 0.369(32.0) + 0.631(28.02) = 29.5 \quad \text{Ans}$$

Or by Eq (7-6),

$$M = \frac{m}{n} = \frac{25}{0.8475} \\ = 29.5 \quad \text{Ans}$$

*c* The specific gas constant is found by Eq (7-4)

$$R = \frac{R_0}{M} = \frac{10.73}{29.5} = 0.3637 \frac{\text{psia ft}^3}{\text{lb}_m \text{ R}} \quad \text{Ans}$$

*d* The volume of the mixture is also the volume of each component

$$V = \frac{n R_0 T}{p} = \frac{n_O R_0 T}{p_O} = \frac{n_N R_0 T}{p_N} = \frac{m R T}{p} \\ V = \frac{0.8475(10.73)(520)}{50} = 94.5 \text{ ft}^3 \quad \text{Ans}$$

The density of the mixture is

$$\rho = \frac{1}{v} = \frac{p}{R_0 T} = \frac{50}{10.73(520)} = 0.00896 \text{ mole/ft}^3 \quad \text{Ans}$$

and since

$$M = 29.5$$

$$\rho = (29.5 \text{ lb}_m/\text{mole})(0.00896 \text{ mole/ft}^3) = 0.264 \text{ lb}_m/\text{ft}^3 \quad \text{Ans}$$

*e* The partial pressures are found by Eq (10-7)

$$p_i = x_i p \\ p_O = 0.369(50) = 18.45 \text{ psia} \quad \text{Ans} \\ p_N = 0.631(50) = 31.55 \text{ psia} \quad \text{Ans} \\ \underline{50.00 \text{ psia}}$$

and the partial volumes by Eq (10-9)

$$\begin{aligned} V_i &= x_i V \\ V_{O_2} &= 0.369(94.5) = 34.85 \text{ ft}^3 & \text{Ans} \\ V_{N_2} &= 0.631(94.5) = 59.65 \text{ ft}^3 & \text{Ans} \\ & \quad \underline{94.5 \text{ ft}^3} \end{aligned}$$

**10-3. Volumetric and Gravimetric Analyses.** The components of a mixture are reported as volume or mass fractions of the entire mixture. The analysis based upon the measurement of volumes is called the *volumetric analysis* while the analysis based upon measurements of mass is called the *gravimetric analysis*.

Experimentally, the volumetric analysis<sup>1</sup> is usually made on a sample of the mixture at atmospheric pressure and temperature, and the volumes of the components are also measured at these conditions. Since the pressure is low, the component gases should behave as perfect gases, and the volume analysis should be directly proportional to the partial volumes

$$V = V_a + V_b + V_c \Big]_{p,T}$$

and by Eq. (10-9)

$$\begin{aligned} x_i &= \frac{n_i}{n} = \frac{V_i}{V} = \text{volume fraction of component } i \\ \frac{V_i}{V} \times 100 &= \text{volume per cent of component } i \end{aligned}$$

The mass or gravimetric analysis reports each component on a mass basis

$$\begin{aligned} m &= m_a + m_b + m_c \\ \frac{m_i}{m} &= \text{mass fraction of component } i & (10-10) \\ \frac{m_i}{m} \times 100 &= \text{mass per cent of component } i \end{aligned}$$

The mass analysis may also be an *ultimate analysis*; here the mass fractions are not for the *components* of the mixture but, rather, for the basic chemical elements that make up the components (that is, the *constituents* of the mixture).

**Example 2:** A gas analyzes by volume 12 per cent  $\text{CO}_2$ , 4 per cent  $\text{O}_2$ , and the remainder  $\text{N}_2$ . Determine the gravimetric analyses

<sup>1</sup> See Art 11-3

**Solution:**

Volumetric per cent + 100 = mole fraction

Mole fraction  $\times M$  = relative mass

Component	Volumetric per cent	Mole fraction	$M$	Relative mass $\left(\frac{\text{lb}_m \text{ component}}{\text{mole mixture}}\right)$
CO <sub>2</sub>	12.0	0.12	44.0	5.28
O <sub>2</sub>	4.0	0.04	32.0	1.28
N <sub>2</sub>	84.0	0.84	28.02	23.52
	100.0	1.00		30.08 or $M$ for mixture

Note that the average molecular weight of the mixture is obtained by adding the figures in the last column of the table

The gravimetric analysis for the components is

$$\frac{m_{\text{CO}_2}}{m} = \frac{5.28}{30.08} = 0.175 \text{ or } 17.5 \text{ per cent} \quad \text{Ans.}$$

$$\frac{m_{\text{O}_2}}{m} = \frac{1.28}{30.08} = 0.043 \text{ or } 4.3 \text{ per cent} \quad \text{Ans.}$$

$$\frac{m_{\text{N}_2}}{m} = \frac{23.52}{30.08} = 0.782 \text{ or } 78.2 \text{ per cent} \quad \text{Ans.}$$

$$\frac{1.000}{100.0} \text{ per cent}$$

The ultimate analysis for the constituents is

Carbon in carbon dioxide  $\frac{12}{44} \times 5.28 = 1.44$  and  $\frac{1.44}{30.08}$   
 is 0.0478, or 4.78 per cent C      *Ans.*

Oxygen in carbon dioxide  $\frac{32}{44} \times 5.28 = 3.84$   
 Oxygen in gas = 1.28

Total oxygen = 5.12 and  $\frac{5.12}{30.08}$   
 is 0.1702, or 17.02 per cent O      *Ans.*

Nitrogen in gas = 23.52 and  $\frac{23.52}{30.08}$   
 is 0.782, or 78.2 per cent N      *Ans.*  
 Total 100.0 per cent

**10-4. The Properties of the Perfect-gas Mixture.** A mixture of perfect gases is characterized by the complete indifference of each component to the presence of other gases. For example, the pressure of the mixture is but the sum of the component or partial pressures

$$p = p_a + p_b + p_c + \dots \quad (10-6)$$

In similar manner, the internal energy (or enthalpy, or heat capacity, or entropy) of the mixture is equal to the sum of the internal energies

of the components; each component is considered to exist alone in the mixture volume, and the value of the whole is equal to the sum of the values for the parts.

$$nu = n_a u_a + n_b u_b + n_c u_c + \dots \Big]_{T,V} \quad (10-11a)$$

$$nh = n_a h_a + n_b h_b + n_c h_c + \dots \Big]_{T,V} \quad (10-12a)$$

$$nc = n_a c_a + n_b c_b + n_c c_c + \dots \Big]_{T,V} \quad (10-13)$$

$$ns = n_a s_a + n_b s_b + n_c s_c + \dots \Big]_{T,V} \quad (10-14a)$$

In the above equations, substitution of mass  $m$  can be made for moles  $n$ , and the properties of the mixture will be based on a mass unit such as the pound (of course, the values of the properties  $u$ ,  $h$ ,  $c$ , and  $s$  must also be in pound mass units).

These equations specify that the properties of the components should be evaluated at the temperature and volume of the mixture, for each component occupies the entire volume. But for perfect gases the properties of internal energy, enthalpy, and heat capacity are dependent only upon temperature, and, therefore, the volume need be considered only when Eqs. (10-11a), (10-12a), and (10-13) are arbitrarily extended to evaluate mixtures of real gases (It should be remembered, however, that the entropy of a perfect, or real, gas is not dependent on temperature alone)

The changes during a process of the properties of internal energy, enthalpy, and entropy of the mixture are of importance. Upon differentiating Eqs. (10-11a), (10-12a), and (10-14a) and dividing by  $n$ , the moles of mixture (and the division restricts the following equations to mole units),

$$du = x_a du_a + x_b du_b + x_c du_c + \dots \quad (10-11b)$$

$$dh = x_a dh_a + x_b dh_b + x_c dh_c + \dots \quad (10-12b)$$

$$ds = x_a ds_a + x_b ds_b + x_c ds_c + \dots \quad (10-14b)$$

Introducing the perfect-gas relationships

$$du = c_v dT \quad (7-7)$$

$$dh = c_p dT \quad (7-8)$$

into Eqs. (10-11b) and (10-12b) yields

$$du = (x_a c_{va} + x_b c_{vb} + x_c c_{vc}) dT \quad (10-11c)$$

$$dh = (x_a c_{pa} + x_b c_{pb} + x_c c_{pc}) dT \quad (10-12c)$$

Equation (10-14b) can be modified by the perfect-gas relationships:

$$ds_i = c_{v,i} \frac{dT}{T} + R_0 \frac{dv_i}{v_i} \quad (8-3)$$

$$ds_i = c_{p,i} \frac{dT}{T} - R_0 \frac{dp_i}{p_i} \quad (8-4)$$

$$ds_i = c_{p,i} \frac{dv_i}{v_i} + c_{v,i} \frac{dp_i}{p_i} \quad (8-6)$$

For example, when Eq. (8-4) is substituted in Eq. (10-14b) (considering a mixture of only two components),

$$ds = x_a \left( c_{pa} \frac{dT}{T} - R_0 \frac{dp_a}{p_a} \right) + x_b \left( c_{pb} \frac{dT}{T} - R_0 \frac{dp_b}{p_b} \right) \quad (a)$$

but from Eq. (10-7)

$$p_i = x_i p \quad \text{and} \quad \frac{dp_i}{dp} = x_i = \frac{p_i}{p} \quad \text{therefore} \quad \frac{dp_i}{p_i} = \frac{dp}{p} \quad (b)$$

Substituting Eq. (b) in Eq. (a) gives

$$ds = (x_a c_{pa} + x_b c_{pb}) \frac{dT}{T} - R_0 \frac{dp}{p} \quad (10-15)$$

Equations (8-3) and (8-6) can be treated in similar manner, noting that

$$\frac{dv_i}{v_i} = \frac{dv}{v} \quad \text{because } n_i v_i = V = n v$$

to yield

$$ds = (x_a c_{va} + x_b c_{vb}) \frac{dT}{T} + R_0 \frac{dv}{v} \quad (10-16)$$

$$ds = (x_a c_{pa} + x_b c_{pb}) \frac{dv}{v} + (x_a c_{va} + x_b c_{vb}) \frac{dp}{p} \quad (10-17)$$

Of course, these results could have been anticipated. Equations (10-15), (10-16), and (10-17) merely show that, after the heat capacities of the mixture have been determined, the mixture can be treated as if it were a single-component system. Such a procedure has already been followed in Chap. VIII, where air, which is a gas mixture, was the main substance studied.

**Example 3:** A mixture of 1 mole of oxygen and 2 moles of nitrogen is confined in a tank at a temperature of 86.6 F and a pressure of 12.7 psia. Determine the entropy of the mixture if each component is assigned a datum state value of zero entropy at 1 atm and 0 F.

**Solution:** The mole fractions are

$$x_O = \frac{1}{3} \quad x_N = \frac{2}{3}$$

and the partial pressures

$$p_O = \frac{1}{3}(12.7) = 4.23 \text{ psia} \quad p_N = \frac{2}{3}(12.7) = 8.46 \text{ psi}$$

From Table VI (Appendix),  $M_{c_p}$  is

$$c_{pO} = 7.01 \text{ Btu/mole R} \quad c_{pN} = 6.94 \text{ Btu/mole R}$$

Equation (8-4) can be used for each component

$$\begin{aligned} ds_i &= c_{p_i} \frac{dT}{T} - R_0 \frac{dp_i}{p_i} \\ s_O = \Delta s_O &= 7.00 \ln \frac{546.6}{460} - 1.986 \ln \frac{4.23}{14.7} \\ &= 1.21 + 2.48 \\ &= 3.69 \text{ Btu/mole R} \\ s_N = \Delta s_N &= 6.94 \ln \frac{546.6}{460} - 1.986 \ln \frac{8.46}{14.7} \\ &= 1.202 + 0.318 \\ &= 1.52 \text{ Btu/mole R} \end{aligned}$$

With these values substituted in Eq. (10-14a),

$$\begin{aligned} S &= ns = n_O s_O + n_N s_N \\ &= 1(3.69) + 2(1.52) = 6.73 \text{ Btu/R} \quad \text{Ans} \end{aligned}$$

**Example 4.** The mixture in Example 3 is cooled at constant volume to a temperature of 50 F. Determine the change in internal energy and in entropy for the mixture.

**Solution:** From Table VI (Appendix),  $M_{c_v}$  is

$$c_{vN} = 4.97 \text{ Btu/mole R} \quad c_{vO} = 5.02 \text{ Btu/mole R}$$

and by Eq. (10-11c) written in the form

$$\begin{aligned} n\Delta u &= (n_N c_{vN} + n_O c_{vO})(T_2 - T_1) \\ &= [2(4.97) + 1(5.02)](-36.6) = -547 \text{ Btu} \quad \text{Ans} \end{aligned}$$

The change in entropy for the mixture is found by Eq. (10-16) integrated for constant-valued heat capacities

$$\begin{aligned} n\Delta s &= (n_O c_{vO} + n_N c_{vN}) \ln \frac{T_2}{T_1} + 0 \\ &= [1(5.02) + 2(4.97)] \ln \frac{510}{546.6} = -1.012 \text{ Btu/R} \end{aligned}$$

**10-5. The Irreversible Mixing Process.**<sup>1</sup> Suppose that several gases, all at the same temperature and pressure, are to be mixed together. For example, in an isolated system each gas could occupy a

<sup>1</sup> The reversible mixing process is introduced (indirectly) in Art. 11-13.



separate partitioned space in a large insulated tank; when the partitions are removed, the gases will individually expand to fill the entire volume. For real gases, such an adiabatic mixing process is not necessarily either an isothermal or a constant-pressure process. But when perfect gases are mixed, each gas undergoes a free expansion to the total volume and to its partial pressure in the mixture, the total pressure remains unchanged at the common initial value for the unmixed components because a free expansion of a perfect gas does not change the temperature (Art 7-3). For this reason, mixing does not affect the values of internal energy, enthalpy, or heat capacity for the component gases because these properties are functions only of temperature. However Eq (8-3) shows that the entropy of each component will increase during the free expansion, and thus from Eq. (10-14b) the entropy change of mixing is positive. This increase is to be expected because mixing is an irreversible process; whenever an irreversible process occurs, the entropy of the isolated system will increase (Art 5-12). Moreover, if the temperatures of the gases before mixing are unequal, the irreversibility of mixing is increased as shown by the loss in availability (Example 8, Chap V).

**Example 5:** A mole of oxygen at 30 psia and 60 F is in a container that is connected through a valve to a second container filled with two moles of nitrogen at 10 psia and 100 F. The valve is opened, and adiabatic mixing occurs. Determine the equilibrium temperature and pressure of the mixture.

**Solution:** For this isolated system, the First Law shows that the change in internal energy is zero

$$Q - W = \Delta U = 0$$

Values of  $M\bar{c}_v$  from Table VI (Appendix) are substituted in Eq (10-11c) and the equilibrium temperature is computed

$$\begin{aligned} n\Delta u &= n_{O_2}(\Delta T)_{O_2} + n_{N_2}(\Delta T)_{N_2} = 0 \\ 1(5.02)(t - 60) + 2(4.97)(t - 100) &= 0 \\ t &= 86.6 \text{ F} \quad \text{Ans} \end{aligned}$$

The pressure is found from the perfect-gas equation of state after the volumes of the tanks have been computed

$$\begin{aligned} pV &= nR_oT \\ V_{O_2} &= \frac{1(10.73)(520)}{30} = 186.2 \text{ ft}^3 \\ V_{N_2} &= \frac{2(10.73)(560)}{10} = 1,203.0 \text{ ft}^3 \\ \text{Total} &= 1,389.2 \text{ ft}^3 \end{aligned}$$

The mixture pressure is

$$p = \frac{nR_oT}{V} = \frac{3(10.73)(546.6)}{1,389.2} = 12.7 \text{ psia} \quad \text{Ans}$$

**Example 6:** Compute the change in entropy for each gas and for the mixing process in Example 5

**Solution:** The change in entropy of each component is found by Eq (8-3)

$$\Delta s = c_v \ln \frac{T_2}{T_1} + R_0 \ln \frac{v_2}{v_1}$$

$\Delta s = \Delta s$  from change in temperature +  $\Delta s$  from change in volume

For the oxygen

$$\begin{aligned} n_O \Delta s_O &= 1(5.02) \ln \frac{546.6}{520} + 1.986 \ln \frac{1,389.2}{186.2} \\ &= 0.246 + 3.985 \\ &= +4.231 \text{ Btu/R} \quad \text{Ans} \end{aligned}$$

For the nitrogen

$$\begin{aligned} n_N \Delta s_N &= 2(4.97) \ln \frac{546.6}{560} + (2)1.986 \ln \frac{1,389.2}{1203} \\ &= -0.236 + 0.556 \\ &= +0.320 \text{ Btu/R} \quad \text{Ans} \end{aligned}$$

The increase in entropy for the process is

$$\Sigma n \Delta s = 4.231 + 0.320 = +4.551 \text{ Btu/R} \quad \text{Ans} \quad \bullet$$

This can be divided into two parts, that part caused by the temperature equalization and that part caused by the expansion (mixing)

$$\begin{aligned} \Sigma n \Delta s &= (+0.246 - 0.236) + (3.985 + 0.556) \\ &= +0.01 + 4.541 = +4.551 \text{ Btu/R} \end{aligned}$$

**10-6. The Isentropic Process.** After the properties of the gas mixture have been determined, analysis of state changes during a process can be made in the same manner as for a single-component system. The isentropic process is of special interest. Note that instantaneous values of the component heat capacities can be substituted in Eq (10-17), and the equation will integrate into the familiar form  $pv^k = C$ . If greater accuracy is desired, mean values of the heat capacities can be used in determining  $k$ , as illustrated in Example 9 Chap. VIII; or better, Eqs (10-15) and (10-16) can be integrated in the manner illustrated in Art. 8-6.

It is well to note that the isentropic process *for the mixture* does not necessarily dictate an isentropic process *for each component* but, rather, that

$$\Delta S_{\text{mixture}} = 0 \quad (a)$$

and, therefore, for a two-component mixture,

$$\Delta S_a + \Delta S_b = 0 \quad (b)$$

Consider that the derivation of Eq (10-15) shows that

$$ds_{\text{mix}} = c_{p \text{ mix}} \frac{dT}{T} - R_0 \frac{dp}{p} \quad (c)$$

$$ds_a = c_{pa} \frac{dT}{T} - R_0 \frac{dp}{p} \quad (d)$$

$$ds_b = c_{pb} \frac{dT}{T} - R_0 \frac{dp}{p} \quad (e)$$

If it is premised that the components, as well as the mixture, are to be isentropically compressed or expanded, inspection of the above equations decrees this is possible only if

$$c_{p \text{ mix}} = c_{pa} = c_{pb}$$

Therefore,

$$\left\{ \begin{array}{l} k_{\text{mix}} = k_a = k_b \end{array} \right.$$

The other alternative for satisfying Eqs (a) and (b) would be that the entropy of one component increased while the entropy of the second component decreased. In a compression process (that is,  $T_2 > T_1$ ,  $p_2 > p_1$ ), suppose that  $\Delta S_a$  is positive (+); then,  $\Delta S_b$  must be negative (-), and Eqs. (c), (d), and (e) show for this case that

$$c_{pa} > c_{pb}$$

Then

$$k_a < k_b$$

because  $c_p - c_v = R_0$  (a constant)

**Example 7.** A mixture of 1 lb<sub>m</sub> air and 0.94 lb<sub>m</sub> steam has a pressure of 50 psia and a temperature of 250 F. If this mixture is isentropically compressed to 100 psia, find (a) the final temperature and (b) the change in entropy for each component.

**Solution:** a. The mole fractions of each component in the mixture are

$$x_a = \frac{(1/29)}{(1/29) + (0.94/18)} = 0.403 \quad x_w = 1.0 - x_a = 0.597$$

Equation (10-15), for the isentropic process, is

$$ds = (x_a c_{pa} + x_w c_{pw}) \frac{dT}{T} - R_0 \frac{dp}{p} = 0$$

The heat capacities will be assumed to be constants, for simplicity, with values selected from Table VI (Appendix)

$$\begin{aligned}
 [0.403(6.96) + 0.597(8.01)] \ln \frac{T_2}{T_1} &= R_0 \ln \frac{p_2}{p_1} \\
 7.59 \frac{\text{Btu}}{\text{mole R}} \ln \frac{T_2}{T_1} &= 1.986 \frac{\text{Btu}}{\text{mole R}} \ln \frac{p_2}{p_1} \quad (f) \\
 \frac{T_2}{T_1} &= \left( \frac{p_2}{p_1} \right)^{0.262} \\
 T_2 &= 710(2)^{0.262} \\
 T_2 &= 851 \text{ R} \quad \text{Ans} \\
 t_2 &= 391 \text{ F} \quad \text{Ans}
 \end{aligned}$$

Note that Eq (f) is equivalent to

$$\begin{aligned}
 c_{p \text{ mix}} \ln \frac{T_2}{T_1} &= R_0 \ln \frac{p_2}{p_1} \\
 \frac{T_2}{T_1} &= \left( \frac{p_2}{p_1} \right)^{\frac{R_0}{c_p}} = \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}}
 \end{aligned}$$

Hence, the average  $k$  for this mixture is equal to

$$\begin{aligned}
 \frac{k-1}{k} &= 0.262 \\
 k &= 1.355
 \end{aligned}$$

*b* The change in specific entropy of the air equals

$$\begin{aligned}
 \Delta s_a &= c_{pa} \ln \frac{T_2}{T_1} - R_0 \ln \frac{p_2}{p_1} \\
 &= (6.96) \ln \frac{851}{710} - 1.986 \ln 2 \\
 \Delta s_a &= -0.105 \text{ Btu/mole R} \quad \text{Ans}
 \end{aligned}$$

and the total change in entropy of the air is

$$\Delta S_a = n \Delta s_a = -0.00362 \text{ Btu/R} \quad \text{Ans}$$

The change in entropy of the water vapor is equal to the change in entropy of the air but of opposite sign

$$\Delta S_w = +0.00362 \text{ Btu/R} \quad \text{Ans}$$

and therefore the change in specific entropy of the water vapor is

$$\Delta s_w = +0.0651 \text{ Btu/mole R} \quad \text{Ans}$$

**10-7. Gas and Vapor Mixtures.** When a liquid is placed in a greater space than its volume, it will evaporate as a vapor into the space above the liquid. This is because the molecules within the liquid move at various velocities; the higher velocity molecules have sufficient energy to overcome the surface restraint and leave the liquid. When the liquid is confined in a closed volume, vapor molecules will strike the liquid surface and be condensed or held by the potential attractive forces of the liquid. Thus, the pressure exerted

by the vapor will assume an equilibrium and maximum value when the rate of vaporization of liquid is balanced by the rate of condensation of vapor. For this equilibrium between *saturated* liquid and *saturated* vapor, the pressure is called the *vapor pressure*, and it is a function of the temperature (Fig 6-2). (As commonly stated, the boiling temperature of the liquid is controlled by the pressure.) The vapor pressure is independent of the relative amounts of vapor and liquid present because both the rate of vaporization and the rate of condensation are proportional to the liquid surface; changing the area of the liquid surface will change the time for reaching equilibrium, but such a change will not affect the equilibrium pressure.

At low pressures, other gases than the vapor from the liquid can be present in the confined space without seriously interfering with the molecular activities of vaporization and condensation. Because of this fact the vapor-pressure-temperature relationship for the pure substance can be applied to a low-pressure system of one liquid component and several gaseous components to predict the maximum partial pressure of the vapor. In this instance the mixture of gases is commonly said to be *saturated* with the vapor from the liquid component, although, to be precise, it is the vapor and the liquid which are saturated. If the temperature of this mixture is raised, the liquid may disappear and, for any additional increase in temperature, the saturated vapor will be *superheated*. Here, no liquid component is present—only gases, hence, the partial pressure of the superheated vapor is proportional to its mole fraction.

**Example 8:** A pound of air saturated with water vapor is in a tank at a temperature of 250 F and a pressure of 50 psia. Determine the volume of the tank and the amount of water vapor present in the mixture.

**Solution:** The vapor pressure and specific volume of the saturated vapor are found from the Steam Tables for a temperature of 250 F. (Here the subscript *s* will be used instead of *w* because the water vapor is saturated.)

$$t = 250 \text{ F} \quad p_s = 29.825 \text{ psia} \quad v_s = v_g \text{ of the Steam Tables} = 13.821 \text{ ft}^3/\text{lb}_m$$

The pressure of the air is found by Dalton's law

$$p = p_a + p_s \quad p_a = 50 - 29.825 \\ = 20.175 \text{ psia}$$

The volume of the tank is the volume occupied by the air

$$pV = nRT \quad V = \frac{15(10.73)(710)}{20.175} \\ V = 13.02 \text{ ft}^3 \quad \text{Ans}$$

This volume is also the volume occupied by the water vapor

$$\frac{V}{v_s} = m_s \quad m_s = \frac{13.02}{13.821} = 0.94 \text{ lb}_m \text{ steam} \quad \text{Ans}$$

(Note that these data are the same as in Example 7)

The answer can be closely checked by Eq (10-7)

$$x_s = \frac{p_s}{p} = \frac{29.825}{50} = 0.597$$

and by Eq (10-3)

$$x_s = \frac{n_s}{n_s + n_a} = \frac{m_s/18}{m_s/18 + 1/29} = 0.597$$

$$m_s = 0.922 \text{ lb}_m \quad \text{Ans.}$$

**Example 9:** Ethyl alcohol is to be used in an automobile carburetor that is adjusted to give a 9 to 1 air-fuel ratio (a mass ratio). If the temperature in the manifold is 60 F and the pressure is atmospheric, what percentage of the alcohol will be evaporated, assuming that equilibrium between vapor and liquid is reached? (Vapor pressure of the alcohol at 60 F is 0.64 psia, and its molecular weight is 46)

**Solution:**

$$x_s = \frac{p_s}{p} = \frac{0.64}{14.7} = 0.0435 \quad (10-7)$$

$$x_s = \frac{n_s}{n_s + n_a} = \frac{m_s/46}{(m_s/46) + (9/29)} = 0.0435 \quad (10-3)$$

$$m_s = 0.65 \text{ lb}_m$$

Hence for every pound of liquid fuel metered by the carburetor, 0.65 lb<sub>m</sub> should be evaporated in the manifold, or 65 per cent vaporization under ideal conditions. *Ans*

In the actual engine a lesser amount is vaporized because sufficient time is not available to allow phase equilibrium to be reached.

**Example 10.** A mixture contains 1 lb<sub>m</sub> of dry air and 0.01 lb<sub>m</sub> of water at a pressure of 20 psia and a temperature of 80 F. Determine the partial pressure of the water vapor.

**Solution:** Here whether or not the air is saturated with water vapor is unknown. If it were saturated, the pressure of the vapor would be (Steam Tables: 80 F)

$$p_s = 0.5069 \text{ psia}$$

and this is the maximum pressure that water vapor can exert at 80 F. On the other hand, if the 0.01 lb<sub>m</sub> of water were superheated vapor, its partial pressure would be proportional to the mole fraction

$$p_w = x_w p = \frac{0.01/18}{(0.01/18) + (1/29)} 20 = 0.318 \text{ psia} \quad \text{Ans.}$$

Since this pressure is less than the saturated pressure, the vapor must be superheated. Thus, for a temperature of 80 F a greater amount of water vapor than 0.01 lb<sub>m</sub> is required to saturate 1 lb<sub>m</sub> of air (and so raise the pressure to the limiting value of 0.5069 psia).

**10-8. Psychrometric Principles.<sup>1</sup>** Dry air is a mixture of gases that has a representative volumetric analysis in per cent as follows: oxygen, 20.99; nitrogen, 78.03; argon, 0.94 including traces of the rare gases neon, helium, and krypton, carbon dioxide, 0.03; and hydrogen, 0.01. For most calculations it is sufficiently accurate to consider dry air as consisting of 21 per cent of oxygen and 79 per cent of inert gases taken as nitrogen (3.76 parts  $N_2$  to 1 part  $O_2$  by volume)

TABLE 10-1 — MASS ANALYSIS OF DRY AIR

Gas	Volumetric analysis, %	Mole fraction	Molecular weight	Relative ( $\frac{\text{lb}_m \text{ component}}{\text{mole mixture}}$ )
$O_2$	20.99	0.2099	32.00	6.717
$N_2$	78.03	0.7803	28.016	21.861
A	0.94	0.0094	39.944	376
$CO_2$	0.03	0.0003	44.003	013
$H_2$	0.01	0.0001	2.016	
	100.00	1.0000		28.967 = M for air

**Dew Point** An important component of the usual air mixture is water vapor existing either as saturated or as superheated steam. The mixture can be cooled at constant pressure, and, if the water vapor is superheated, each component will

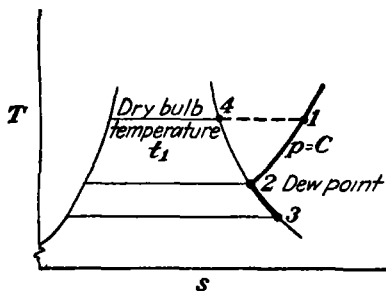


FIG 10-1 Relationship of dry-bulb and dew point temperatures

be cooled at constant partial pressure because the composition of the gaseous mixture remains constant. With continued cooling, the water vapor will reach the saturated state, and any further decrease in temperature will cause condensation and thus a change in composition of the gaseous phase. The temperature that marks the appearance of liquid water is called the *dew point*. In

Fig 10-1 the path of the cooling process for the water-vapor component is shown on the  $T$ - $s$  diagram. At state 1 the vapor is superheated at a temperature called the *dry-bulb* temperature, which can be measured with the usual thermometer. Cooling at constant partial pressure occurs from state 1 to state 2. At state 2, the *dew point*, the water vapor is saturated. If the temperature of the air is lowered beneath

<sup>1</sup> In this section the terminology of reference 1 has been adopted wherever feasible, similarly, all empirical constants have been obtained from this source

the dew point, the air remains saturated, although the partial pressure of the water vapor progressively decreases because of condensation while the state changes from 2 to 3. Note that the dew-point temperature allows the vapor pressure of the superheated vapor to be found from the Steam Tables. The partial pressure of the saturated vapor at the dew point is also the partial pressure of the superheated vapor at state 1.

**Relative Humidity** The *relative humidity*  $\phi$  is best defined as the ratio of the actual partial pressure of the vapor to the saturated partial pressure of the vapor at the same temperature

$$\phi = \left. \frac{p_w}{p_s} \right]_T$$

where subscript  $w$  = water vapor

subscript  $s$  = saturated water vapor

In Fig. 10-1, the relative humidity of the superheated vapor in the mixture at  $t_1$  is the ratio of the partial pressure at state 1 (or 2) to the partial pressure at state 4. Since the perfect-gas laws are quite accurate at the low pressures encountered with atmospheric air,  $\phi$  can be expressed as, noting that the temperature is the same at states 1 and 4,

$$\phi = \frac{p_w}{p_s} = \frac{R_w T / v_w}{R_w T / v_s} = \frac{v_s}{v_w} = \frac{\rho_w}{\rho_s} \quad (10-18)$$

As shown by Eq. (10-18), relative humidity (at low pressures) is the ratio of the density of the steam present in the mixture to the saturation density of steam at the same temperature. When the relative humidity of the mixture is 1.0, the mixture is at the dew point.

**Humidity Ratio—Specific Humidity** The *humidity ratio* or *specific humidity*  $\omega$  is defined as the ratio of the mass of water vapor to the mass of dry air in the mixture

$$\omega = \left. \frac{m_w}{m_a} \right]_{v, T}$$

Thus, a mixture containing 1 lb<sub>m</sub> of dry air would contain  $\omega$  lb<sub>m</sub> of steam, and at low pressure,

$$\omega = \frac{m_w}{m_a} = \frac{\rho_w}{\rho_a} = \frac{p_w / R_w T}{p_a / R_a T} = \frac{p_w}{p_a} \frac{R_a}{R_w} = 0.622 \frac{p_w}{p - p_w} \quad (10-19)$$

( $R_w$  and  $R_a$  are specific gas constants for water vapor and air.) The specific and the relative humidities are related; by Eq. (10-18)

$$p_w = \phi p_s$$



and, upon substitution in Eq. (10-19),

$$\omega = \phi \frac{p_s}{p_a} \frac{R_a}{R_w} = \phi \frac{\rho_s}{\rho_a} = \phi \frac{v_a}{v_s} \quad (10-20)$$

**Example 11:** The temperature in a room is 80 F, and the relative humidity is 30 per cent. Determine (a) the partial pressure of the steam and the dew point, (b) the density of each component, (c) the specific humidity. (Barometer reads 29.92 in Hg.)

**Solution:** a The vapor pressure of saturated steam at 80 F is obtained from the Steam Tables:

$$p_s = 0.5069 \text{ psia} \quad \text{and} \quad v_s = 633.1 \text{ ft}^3/\text{lb}_m$$

Since in this problem the relative humidity is 30 per cent,

$$p_w = \phi p_s = 0.30(0.5069) = 0.15207 \text{ psia} \quad \text{Ans}$$

This partial pressure of the superheated vapor is also the saturation pressure that defines the dew point. Thus, from the Steam Tables

$$t_{\text{dew}} \approx 46 \text{ F} \quad \text{Ans}$$

b The density of the saturated steam at 80 F is

$$\rho_s = \frac{1}{v} = \frac{1}{633.1} = 0.00158 \text{ lb}_m/\text{ft}^3$$

and, since the relative humidity is 30 per cent, by Eq. (10-18)

$$\rho_w = \phi \rho_s = 0.30(0.00158) = 0.000474 \text{ lb}_m/\text{ft}^3 \quad \text{Ans}$$

This answer can be checked by the perfect-gas equation using  $85.6 \frac{\text{ft} \cdot \text{lb}_f}{\text{lb}_m \cdot \text{R}}$  for the specific gas constant

$$\begin{aligned} p v &= R T \\ \rho_w &= \frac{p}{R T} = \frac{0.15207(144)}{85.6(540)} = 0.000474 \text{ lb}_m/\text{ft}^3 \quad \text{Ans} \end{aligned}$$

The density of the dry air is similarly found

$$\begin{aligned} p_a &= p - p_w \\ &= 14.696 - 0.1521 \\ &= 14.544 \text{ psia} \\ \rho_a &= \frac{p_a}{R_a T} = \frac{14.544(144)}{53.3(540)} = 0.0729 \text{ lb}_m/\text{ft}^3 \quad \text{Ans} \end{aligned}$$

c The specific humidity is found by Eq. (10-19)

$$\omega = \frac{\rho_w}{\rho_a} = \frac{0.000474}{0.0729} = 0.0065 \quad \text{Ans}$$

or more expressively

$$\omega = 0.0065 \frac{\text{lb}_m \text{ steam}}{\text{lb}_m \text{ air}} \quad \text{Ans}$$

**Example 12:** Atmospheric air at 20 F and 60 per cent relative humidity is conditioned to 80 F and 50 per cent relative humidity. Determine the amount of water added to the air. (Barometer reads 29.92 in Hg.)

**Solution :** The pressure of saturated vapor at 20 F is found in the Steam Tables

$$p_s = 0.0505 \text{ psia}$$

The partial pressure of the water vapor initially in the atmosphere is

$$\begin{aligned} p_w &= \phi p_s \\ &= 0.60(0.0505) = 0.0303 \text{ psia} \end{aligned}$$

and by Eq (10-19) the initial humidity ratio is

$$\begin{aligned} \omega_1 &= 0.622 \frac{p_w}{p - p_w} = 0.622 \frac{0.0303}{14.696 - 0.0303} \\ &= 0.001288 \frac{\text{lb}_m \text{ steam}}{\text{lb}_m \text{ dry air}} \end{aligned}$$

Each of the above steps is repeated for the air after conditioning to 80 F

$$\begin{aligned} p_s &= 0.5067 \text{ psia} \\ p_w &= \phi p_s = 0.50(0.5067) = 0.2533 \text{ psia} \\ \omega_2 &= 0.622 \frac{p_w}{p - p_w} = 0.622 \frac{0.2533}{14.443} \\ \omega_2 &= 0.0109 \frac{\text{lb}_m \text{ steam}}{\text{lb}_m \text{ dry air}} \end{aligned}$$

The change in moisture content of the air during the process equals

$$\begin{aligned} \omega_2 - \omega_1 &= 0.0109 - 0.001288 \\ &= 0.009612 \frac{\text{lb}_m \text{ water}}{\text{lb}_m \text{ dry air}} \quad \text{Ans} \end{aligned}$$

Expressed in grains where

$$\begin{aligned} 7,000 \text{ grains} &= 1 \text{ lb}_m \\ \omega_2 - \omega_1 &= 0.009612(7,000) = 67.284 \frac{\text{grains water}}{\text{lb}_m \text{ dry air}} \quad \text{Ans} \end{aligned}$$

**10-9. Multiple-stream Steady-flow Processes.** The conditioning of large quantities of air or water invariably demands a steady-flow

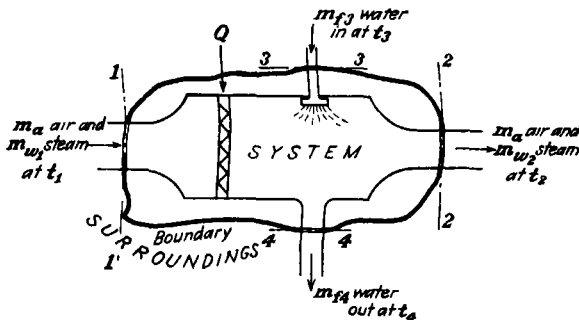


FIG 10-2 General steady-flow air-conditioning system

process, and, in most instances, more than one flow path will be present In Fig 10-2, air with its contained moisture enters a system and leaves

with a greater or lesser amount of vapor. Because of this humidification or dehumidification water must also enter or leave if the process is to be continuous, while the system may or may not be adiabatic. An energy balance can be made for this general system from Eq. (3-6) to yield

$$Q = \Sigma m h_{\text{out}} - \Sigma m h_{\text{in}}$$

and therefore

$$Q \frac{\text{Btu}}{\text{time unit}} = \underbrace{m_a(h_{a2} - h_{a1})}_{\text{dry air}} + \underbrace{(m_{w2}h_{w2} - m_{w1}h_{w1})}_{\text{water vapor}} + \underbrace{(m_{f4}h_{f4} - m_{f3}h_{f3})}_{\text{water}} \quad (10-21a)$$

Upon dividing by  $m_a$  (and changing the units of  $Q$ ), it is found that

$$Q \frac{\text{Btu}}{\text{lb}_m \text{ dry air}} = (h_{a2} - h_{a1}) + (\omega_2 h_{w2} - \omega_1 h_{w1}) + \frac{(m_{f4}h_{f4} - m_{f3}h_{f3})}{m_a} \quad (10-21b)$$

where subscript  $a$  = air

$w$  = water vapor

$f$  = liquid water (although not necessarily saturated)

1 = entrance conditions for air-steam mixture

2 = exit conditions for air-steam mixture

3 = entrance conditions for water

4 = exit conditions for water

The amounts of water entering or leaving the system at 3 and 4 are not equal because a part of the water is either added or taken away from the air mixture. For continuity of mass flow of the water component,

$$\omega_2 - \omega_1 = \frac{m_{f3} - m_{f4}}{m_a} \quad (10-21c)$$

The equations can be simplified by defining the enthalpy of the mixture of 1 lb<sub>m</sub> dry air plus  $\omega$  lb<sub>m</sub> of water vapor to be

$$H \frac{\text{Btu}}{\text{lb}_m \text{ dry air}} = h_a + \omega h_w \quad (10-22)$$

When this identity is substituted in Eq. (10-21b),

$$Q \frac{\text{Btu}}{\text{lb}_m \text{ dry air}} = H_2 - H_1 + \frac{m_{f4}h_{f4} - m_{f3}h_{f3}}{m_a} \quad (10-21d)$$

In some instances, only one flow stream of water is associated with the system, for example, the spray water could be entirely vaporized

by the air and therefore  $m_{f4}$  would be zero. For this case Eq (10-21b) reduces to

$$Q \frac{\text{Btu}}{\text{lb}_m \text{ dry air}} = (h_{a2} - h_{a1}) + (\omega_2 h_{u2} - \omega_1 h_{u1}) - (\omega_2 - \omega_1) h_{f3} \quad (10-23a)$$

$$= H_2 - H_1 - (\omega_2 - \omega_1) h_{f3} \quad (10-23b)$$

because, for continuity of mass flow,

$$m_a(\omega_2 - \omega_1) = m_{f3} \quad (10-23c)$$

The uses for these equations will be illustrated in following articles.

**10-10. Temperature of Adiabatic Saturation (Thermodynamic Wet-bulb Temperature).** A method for measuring humidity will now be analyzed. Consider a process wherein the humidity of air is increased by passing it through an insulated chamber that contains a

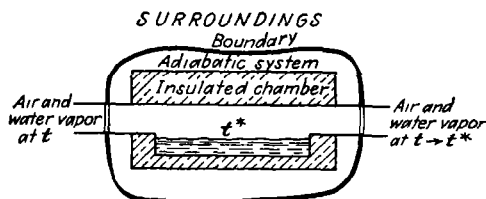


FIG 10-3 Process of adiabatic saturation

large surface of water (Fig 10-3). Here the air is cooled in passing over the water, and the water is cooled as vaporization occurs. For this adiabatic process the water will reach an equilibrium temperature when the thermal energy transferred from the air to the water is equal to the thermal energy required to vaporize the water. This equilibrium temperature ( $t^*$ )<sup>1</sup> is called the *thermodynamic wet-bulb temperature* and, also, the *temperature of adiabatic saturation*, it is the lowest temperature reached by the water in the process of Fig 10-3.

The temperature of adiabatic saturation for water and air is measured quite closely by a *wet-bulb thermometer*. In Fig 10-4, is illustrated a *sling psychrometer* that consists of a wet-bulb and a dry-bulb thermometer. The wet bulb is covered with a wick moistened with water. When the psychrometer is rapidly moved through unsaturated air, water will evaporate from the wick in a manner somewhat similar to the evaporation process in Fig 10-3. By this means the wet- and dry-bulb temperatures of the air are obtained.

Suppose that the insulated chamber of Fig 10-3 is infinitely long,

<sup>1</sup> The asterisk (\*) designates that the property is to be evaluated at the temperature of adiabatic saturation

then, the air leaving the chamber will be at the same temperature as the water, and, moreover, the air will be saturated with water vapor. Thus, as the air passes through the chamber, the *dry-bulb* temperature of the air progressively decreases until the limiting temperature of adiabatic saturation is reached. The *wet-bulb* temperature of the air, however, remains constant at all sections of Fig 10-3 because this temperature is essentially the temperature of adiabatic saturation. The condition of the water vapor as it passes through the chamber is illustrated in Fig 10-5 by path 1-2 (Note that the dew point and the wet-bulb temperatures have quite different values except for the one case of saturated air.)

The system of Fig 10-3 can be converted into a steady-flow system by supplying make-up water at the wet-bulb temperature. Assume that the air

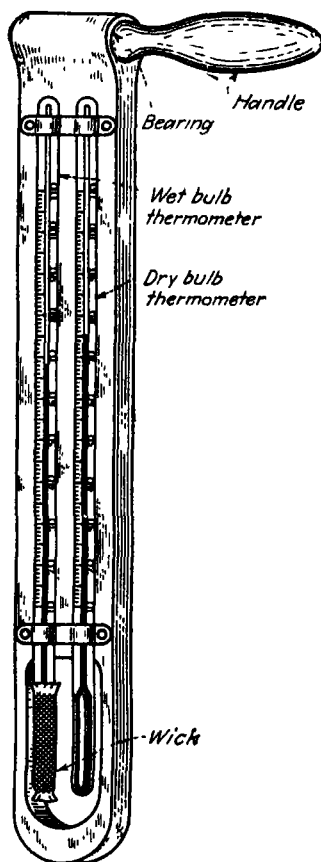


FIG 10-4 Sling psychrometer

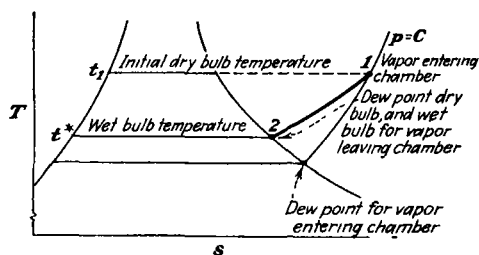


FIG 10-5 State changes of the vapor during the process of adiabatic saturation

leaves the system at the temperature of adiabatic saturation. For this process, when it is noted that

$$Q = 0$$

$$\omega_2(h_{w2} - h_{f3}) = \omega^*(h_a^* - h_f^*) = \omega^*h_{fg}^*$$

$$h_{a2} = h_a^*$$

then Eq (10-23a) can be arranged into the form,

$$\omega = \frac{(h_a^* - h_a) + \omega^*h_{fg}^*}{h_w - h_f^*} \quad (10-24)$$

Equation (10-24) can be used to find the specific humidity of air ( $\omega$ ) since all other terms in the equation can be computed or measured with an apparatus like that in Fig 10-3 or with a sling psychrometer. However, an approximation derived from Eq (10-24) and first proposed by Carrier (1911) is most often used to find humidity (Example 13)

$$p_w = p_s^* - \frac{p - p_s^*}{2,830 - 1.44t^*} (t - t^*) \quad (10-25)$$

An important generalization can be seen by applying Eq (10-23b) to the process of adiabatic saturation

$$H_1 + (\omega^* - \omega_1)h_f^* = H_2^* \quad (10-26a)$$

Since the middle term is relatively insignificant,<sup>1</sup>

$$H_1 \approx H_2^* \quad (10-26b)$$

Equation (10-26b) shows that the total enthalpy of the mixture remains essentially constant during the process of adiabatic saturation. Since the wet-bulb temperature also remains constant during this process, *it can be concluded that the total enthalpy of the air-vapor mixture is a function of the wet-bulb temperature.* This approximation is sufficiently accurate for most meteorological and air-conditioning work.

**Example 13.** Air has a dry-bulb temperature of 80 F and a wet-bulb temperature of 60 F. Determine (a) the relative humidity, (b) the humidity ratio. (Barometer is 14.696 psia.)

**Solution.**

$$a \quad p_w = p_s^* - \frac{p - p_s^*}{2,830 - 1.44t^*} (t - t^*) \quad (10-25)$$

where  $p_s^* = 0.2563$  psia,  $p_s = 0.5069$  psia (Steam Tables 60 and 80 F)

$p = 14.696$  psia

$$p_w = 0.2563 - \frac{14.696 - 0.2563}{2830 - 1.44(60)} (80 - 60)$$

$$= 0.2563 - 0.1052$$

$$= 0.1511 \text{ psia}$$

From Eq (10-18)

$$\phi = \frac{p_w}{p_s} = \frac{0.1511}{0.5069} = 0.30, \text{ or } 30 \text{ per cent} \quad \text{Ans}$$

b From Eq (10-19)

$$\omega = 0.622 \frac{p_w}{p - p_w} = 0.622 \frac{0.1511}{14.545} = 0.00647 \quad \text{Ans}$$

<sup>1</sup> For this reason the make-up water *added* to the adiabatic saturation process can be at a quite different temperature from the wet-bulb temperature without perceptibly changing the final condition of the air.

or Eq (10-24) can be used

$$\omega = \frac{(h_a^* - h_a) + \omega^* h_{fg}^*}{h_w - h_f^*}$$

$$\text{where } \omega^* = 0.622 \frac{0.2563}{14.696 - 0.2563} = 0.0111 \quad (10-19)$$

$$h_{fg}^* = 1059.9 \text{ Btu/lb}_m \text{ (Steam Tables 60 F)}$$

The enthalpy of air at low pressures is quite accurately evaluated by the perfect-gas relation

$$h_a^* - h_a = c_p(t^* - t) = 0.240(t^* - t)$$

(Here, arbitrarily, the datum of zero enthalpy is 0 F) The enthalpy of water vapor at low pressures can be found from tables or from an empirical<sup>1</sup> formula

$$h_w = 1061 + 0.444t = 1096.5 \text{ Btu/lb}_m$$

The enthalpy of subcooled water can be assumed to be equal to the saturated value for the known temperature. However, adequate accuracy is obtained from the approximation

$$\begin{aligned} h &= c_p(t - 32) = 1.0(t - 32) \\ h^* &= (60 - 32) = 28 \text{ Btu/lb}_m \end{aligned}$$

(In these equations, the datum of zero enthalpy is the same as in the Steam Tables 32 F) With these substitutions

$$\begin{aligned} \omega &= \frac{0.240(60 - 80) + 0.0111(1059.9)}{1096.5 - 28} \\ &= 0.0065 \quad \text{Ans} \end{aligned}$$

(Although the datum state for air is different from that for water, only differences in enthalpy appear in the equations, and therefore the datum state is of no significance in the calculations.)

**10-11. The Psychrometric Chart.** Although the properties of the air mixture can be readily calculated, it is more convenient to use a psychrometric chart (Fig V, Appendix). The General Electric chart was constructed for a mixture pressure of 14.696 psia, but it can be used with acceptable accuracy for many calculations even though the real barometric pressure may differ from the standard value. The values on the chart are for a mixture of 1 pound of dry air plus the contained water vapor. Enthalpy ( $H$ ) of the mixture (called *total heat* on the GE chart) is the enthalpy of 1 pound of dry air above a datum of 0 F plus the enthalpy of the water vapor above a datum of 32 F. Note that lines of constant enthalpy are also lines of constant wet-bulb temperatures [see Eq (10-26b) and discussion]

**Example 14:** Repeat Example 11, using the psychrometric chart

**Solution:** Given Air at 80 F and  $\phi = 0.30$

*a* Determine the partial pressure of the water vapor and the dew point

<sup>1</sup> Reference 1

On the GE chart locate 80 F on the abscissa, then ascend vertically to the curved line marked 30 per cent ( $\phi$ ) On the left ordinate scale read

$$p_w = 0.15 \text{ psia} \quad \text{Ans.}$$

compared with 0.152 psia of Example 11 The dew point has the same partial pressure as the superheated vapor Hence, proceed horizontally from  $t = 80$  F,  $\phi = 30$  per cent (or  $p_w = 0.15$  psia), to the saturation curve (which is identified by the equality of the wet- and dry-bulb temperatures

$$t_{\text{dew}} = 46 \text{ F} \quad \text{Ans}$$

which agrees with Example 11

b Determine the density of each component

Note the diagonal lines sloping from left to right marked "Cu-ft per Lb of Dry Air " At  $t = 80$  F,  $\phi = 30$  per cent, read (interpolate)

$$v_a = 13.74 \text{ ft}^3/\text{lb}_m \text{ dry air}$$

and

$$\rho_a = \frac{1}{v_a} = 0.0728 \text{ lb}_m/\text{ft}^3 \quad \text{Ans}$$

compared with 0.0729 lb<sub>m</sub>/ft<sup>3</sup> of Example 11 In this same volume is contained 45 grains of water vapor (scale on left ordinate), and

$$\rho_w = \frac{m_w}{V} = \frac{45}{13.74} = 0.000468 \text{ lb}_m/\text{ft}^3 \quad \text{Ans.}$$

compared with 0.000474 lb<sub>m</sub>/ft<sup>3</sup> of Example 11

c Determine the humidity ratio

The specific humidity is directly the mass of water vapor associated with 1 pound of dry air, and, as found in (b),

$$\omega = 45 \frac{\text{grains water}}{\text{lb}_m \text{ dry air}} = 0.00643 \frac{\text{lb}_m \text{ water}}{\text{lb}_m \text{ dry air}} \quad \text{Ans}$$

compared with 0.0065 of Example 11

**Example 15.** Calculate the enthalpy of the mixture of Examples 11 and 14

**Solution:**

$$\begin{aligned} \text{Given } t &= 80 \text{ F} & \phi &= 0.30 & \omega &= 0.00643 \\ H &= h_a + \omega h_w \end{aligned} \quad (10-22)$$

When the equations given in Example 13 are substituted,

$$\begin{aligned} H &= 0.240t + 0.00643(1061 + 0.444t) \\ &= 19.2 + 7.05 \\ &= 26.25 \text{ Btu/lb}_m \text{ dry air} \quad \text{Ans} \end{aligned}$$

Compare with the chart value 26.5 Btu/lb<sub>m</sub> dry air

**10-12. Air-conditioning Applications.** *Adiabatic Mixing* A steady-flow process frequently encountered in air conditioning is the adiabatic mixing of several streams of air to form a conditioned mixture Suppose that two streams of air enter a system and adiabatically mix, and



one stream of air emerges (Fig 10-6) For this system,

$$\Sigma m h_{out} = \Sigma m h_{in} \quad (3-6)$$

and

$$m_{a1}H_1 + m_{a2}H_2 = (m_{a1} + m_{a2})H_3 \quad (10-27)$$

$$m_{a1}\omega_1 + m_{a2}\omega_2 = (m_{a1} + m_{a2})\omega_3 \quad (10-28)$$

Equations (10-27) and (10-28) can be rearranged

$$m_{a1}(H_1 - H_3) = m_{a2}(H_3 - H_2)$$

$$m_{a1}(\omega_1 - \omega_3) = m_{a2}(\omega_3 - \omega_2)$$

and therefore

$$\frac{m_{a1}}{m_{a2}} = \frac{H_3 - H_2}{H_1 - H_3} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3} \quad (10-29a)$$

On the psychrometric chart the final state 3 of the mixture lies on a straight line connecting the initial states of the two streams before

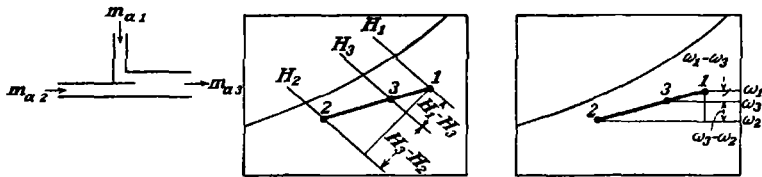


FIG 10-6 Adiabatic mixing process on the psychrometric chart

mixing This is proved by Fig 10-6 and Eqs (10-29) (since the  $H$  and  $\omega$  scales are linear)

$$\frac{\text{line } 2-3}{\text{line } 3-1} = \frac{H_3 - H_2}{H_1 - H_3} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3} = \frac{m_{a1}}{m_{a2}} \quad (10-29b)$$

Moreover, as shown by Eq (10-29b), the final state 3 divides the line into two parts that are in the same ratio as were the two relative masses of *dry air* before mixing

**Example 16:** A stream of 2,000 cfm of saturated air at 50 F is mixed with 1,500 cfm of air at 80 F and 60 per cent relative humidity Determine the final condition of the mixture

**Solution:** From the psychrometric chart

At 50 F (sat)

$$v_a = 13.0 \frac{\text{ft}^3}{\text{lb}_m \text{ dry air}}$$

At 80 F,  $\phi = 0.60$

$$v_a = 13.88 \frac{\text{ft}^3}{\text{lb}_m \text{ dry air}}$$

Hence,

$$m_{a1} = \frac{2,000}{13.0} = 154 \frac{\text{lb}_m \text{ dry air}}{\text{min}}$$

$$m_{a2} = \frac{1,500}{13.88} = 108 \frac{\text{lb}_m \text{ dry air}}{\text{min}}$$

The straight line connecting the two initial states can be divided by the ratio  $\frac{t_1 - t_2}{t_2 - t_3}$ , and point 3 is located.

$$t = 71^\circ \text{F} \quad \phi = 71 \text{ per cent} \quad \text{Ans}$$

**Heating and Cooling without Change in Specific Humidity** If air is heated or cooled without change in moisture content, the path for the process must lie on a horizontal line on the psychrometric chart, such as line 1-2, Fig 10-8. The heat transferred to or from the air is readily found by Eq (10-21a), (10-21b), or (10-21d) for the condition that

$$m_{f3} = m_{f4} = 0$$

**Cooling and Dehumidifying** Suppose that a cooling coil is placed in the air stream, as illustrated in Fig 10-7. One portion of air may

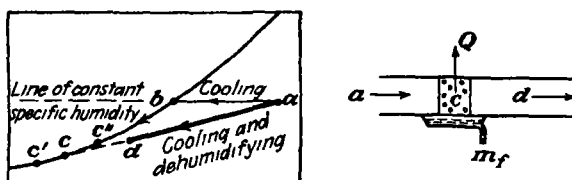


Fig 10-7 Cooling and dehumidifying process on the psychrometric chart

be cooled along path  $ab$  to the dew point, and condensation would then take place as the temperature is reduced from  $b$  to  $c'$  or  $c''$ . A second portion of air may never strike the coil but instead may be cooled by mixing with the first and colder element. Now if the cooling coil is infinitely long, the air will mix together and assume an average end point such as  $c$ . However, in the real system, this saturated state is never reached and the final state of the air stream will be at a point such as  $d$ . Since this entire process involves mixing as well as cooling, point  $d$  will lie on a line between the initial state  $a$  and the theoretical saturation condition  $c$  at the mean surface-temperature of the coil. The heat that must be transferred from this system is evaluated by modifying Eq (10-23b)

Air can be cooled and dehumidified by passing the air stream through a spray or curtain of cold water that is chilled by an external refrigerator to a temperature lower than the dew point of the initial air. The air will be humidified and cooled if the water is supplied at a higher temperature than the dew point of the air stream and, of course, at a lower temperature than the air temperature. These processes can be evaluated by Eq. (10-21a), (10-21b), or (10-21d).

**Evaporation Cooling** If the quantity of water sprayed into an air stream were reduced until no leaving stream of water left the system,

it would be found that the air would be cooled and humidified. The air would be cooled even though the temperature of the entering water was higher than that of the air. In this instance, the heat capacity of the small amount of water that enters the system cannot markedly increase the temperature of the much greater amount of air. But when evaporation occurs and the high latent-heat demands of water are satisfied, a pronounced drop in temperature of the air takes place to

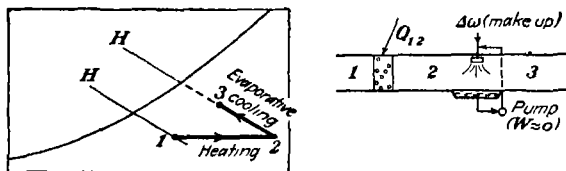


FIG 10-8 The processes of heating without change in specific humidity and evaporative cooling on the psychrometric chart

supply the thermal energy. In a similar manner, if a small amount of very cold water is introduced and entirely evaporated, the chilling effect of the cold water on the hot air is negligibly small in comparison with the thermal demands of vaporization.

In evaporative cooling, a large amount of water is pumped into a spray chamber and constantly recirculated without transfer of heat. Thus, the temperature of the water will gradually decrease and approach as a limit the temperature of adiabatic saturation. To this circulating water must be added make-up water to replace the water vapor that has been formed and carried away by the air. The amount of make-up water will be small; thus, the effect of its temperature, being other than the wet-bulb temperature, on the equilibrium temperature is negligible.

This type of air washer, with recirculating water that is neither heated nor cooled from an external source, is a common means for cooling and humidifying air. The path followed by the air during the cooling is essentially at constant wet-bulb temperature (path 2-3, Fig 10-8), and the energy balance for the process is given by Eq (10-26a). (Note that process 1-2 in Fig 10-8 is quite independent of process 2-3.)

**Example 17:** Air at a temperature of 90 F and 30 per cent relative humidity is cooled in an adiabatic spray humidifier that uses recirculated water. If the process reduces the air temperature by 80 per cent of the original wet-bulb depression, what will be the final condition of the air?

**Solution:** At  $t = 90$  F,  $\phi = 0.30$ , then, from the chart  $t^* = 67.2$  F

$$\text{Original wet-bulb depression} = 90 - 67.2 = 22.8 \text{ F}$$

Then, the temperature reduction is

$$\Delta t = 22.8(0.80) = 18.24 \text{ F}$$

and the dry-bulb temperature equals

$$t = 90 - 18.24 = 71.76 \text{ F} \quad \text{Ans}$$

(The final wet-bulb temperature is the same as the initial value 67.2 F) From the chart

$$\phi = 0.80 \quad \text{Ans}$$

**Cooling Tower.** A cooling tower is often used to cool water by evaporation. At the top of the tower, hot water is sprayed downward through baffles that keep the water in small streams or drops to present large areas for evaporation. Atmospheric air enters the tower at the base and flows upward against the liquid particles; the hot water is cooled, mainly by vaporization of a part of the water, while the air is raised in temperature and also saturated (essentially) with water vapor. Because of the evaporation, the water may be cooled below the dry-bulb temperature of the entering air (but it cannot be cooled below the wet-bulb temperature). Equation (10-21a), (10-21b), or (10-21d) can be directly applied to this adiabatic process by noting that  $Q = 0$ .

**Example 18.** Water is cooled in a cooling tower from a temperature of 100 to 75 F. Air enters the tower at a temperature of 82 F with relative humidity of 40 per cent and leaves at a temperature of 95 F with relative humidity of 98 per cent. Determine (a) the amount of water cooled per pound of dry air and (b) the percentage of water lost by evaporation.

**Solution.** a Equation (10-21d) is best used for solution with  $Q = 0$  and  $m_a = 1 \text{ lb}_m$

$$H_2 - H_1 + m_{f4}h_{f4} - m_{f3}h_{f3} = 0 \quad (a)$$

From the psychrometric chart,

$$\begin{aligned} t = 82 \text{ F} \quad \phi = 40 \text{ per cent} \quad H_1 &= 30 \text{ Btu/lb}_m \text{ dry air} \quad (\text{and } t^* = 65 \text{ F}) \\ \omega_1 &= 65 \text{ grains/lb}_m \text{ dry air} \\ t = 95 \text{ F} \quad \phi = 98 \text{ per cent} \quad H_2 &= 62.2 \text{ Btu/lb}_m \text{ dry air} \\ \omega_2 &= 250 \text{ grains/lb}_m \text{ dry air} \end{aligned}$$

(These values, of course, could have been computed) From Eq (10-21c) for  $m_a = 1 \text{ lb}_m$

$$\begin{aligned} m_{f3} - m_{f4} &= \omega_2 - \omega_1 = 250 - 65 = 185 \text{ grains/lb}_m \text{ dry air} = 0.0264 \\ m_{f3} &= 0.0264 + m_{f4} \end{aligned}$$

The enthalpy of the water can be approximated by the relation

$$\begin{aligned} h_f &= (t - 32) \text{ Btu/lb}_m \\ t = 100 \text{ F} \quad h_{f3} &= 68 \text{ Btu/lb}_m \quad t = 75 \text{ F} \quad h_{f4} = 43 \text{ Btu/lb}_m \end{aligned}$$

Substituting these values in Eq (a),

$$62.2 - 30 + m_{f4}(43) - (0.0264 + m_{f4})68 = 0$$

$$m_{f4} = 1.218 \frac{\text{lb}_m \text{ water}}{\text{lb}_m \text{ dry air}} \quad \text{Ans.}$$

b The percentage of water lost by evaporation is

$$m_{f3} - m_{f4} = \omega_2 - \omega_1 = 0.0264 \frac{\text{lb}_m \text{ water}}{\text{lb}_m \text{ dry air}}$$

or

$$\frac{0.0264}{1.218 + 0.0264} = 0.0212, \text{ or } 2.12 \text{ per cent} \quad \text{Ans}$$

Thus, for every pound of hot water entering the tower, 0.9788 lb<sub>m</sub> of cold water leaves the tower

**10-13. More Detailed Treatment of Mixtures.** The laws of Dalton and Amagat can be proved true only for a mixture of ideal gases because the perfect-gas equation of state is a necessary part of the derivations. However, the philosophy of either law can be applied to a mixture of real gases without demanding that the real gases obey the perfect-gas equation of state. The pressure exerted by each component of a mixture can be computed by methods known to be more exact than the perfect-gas equation, and the total pressure can be premised to be the sum of the component pressures. Thus, Dalton's law of additive pressures,

$$p = p_a + p_b + \cdots p_i \Big]_{T,V} \quad (10-30)$$

is here released from any dependence on the perfect-gas equation of state. It is still assumed that each gas occupies the entire volume of the mixture and exerts a pressure that is totally independent of the pressure of the other components.

In similar manner the law of Amagat can be treated. Here the volume occupied by a component, at the pressure and temperature of the mixture, can be computed by means other than the perfect-gas equation

$$V = V_a + V_b + \cdots V_i \Big]_{p,T} \quad (10-31)$$

Although Dalton's and Amagat's laws will give identical answers for a mixture of perfect gases, the two laws generally yield different answers for real gases. Which of these laws will better predict the properties of a particular and real-gas mixture cannot be definitely stated, although certain generalizations can be attempted. The law of Amagat treats each component at the full mixture pressure, this

procedure implies that each gas in the mixture recognizes the existence of the other gases and engages in molecular collisions and interactions with these components to the same degree as if the gas were entirely homogeneous. Dalton's law treats each gas at a pressure lower than the mixture pressure; this procedure ignores entirely the density of the mixture, which may be high because of the presence of other gases. For these reasons the law of Amagat should be more accurate than Dalton's law (but see Example 19), although it must be realized that both laws are semiempirical. Because most equations of state are explicit in pressure, Dalton's law is easier to apply than Amagat's law, which may require a trial-and-error solution.

**Example 19:** Calculate the pressure exerted by a mixture<sup>1</sup> of 0.396 mole methane and 0.604 mole butane if the volume is 8.518 ft<sup>3</sup> and the temperature is 460° F.

*Ans* 68 atm

**Solution:**

*a* *Law of Additive Pressures* Van der Waals' equation will be used to find the pressure of each component.  
From Table VIII (Appendix)

	<i>a</i>	<i>b</i>
Methane	578.9 atm ft <sup>3</sup> /mole <sup>2</sup>	0.684 ft <sup>3</sup> /mole
Butane	3,675	1.944

$$p = \frac{R_0 T}{v - b} - \frac{a}{v^2} = \frac{n R_0 T}{V - bn} - \frac{an^2}{V^2} \quad \text{where} \quad R_0 = 0.73 \frac{\text{atm ft}^3}{\text{mole } ^\circ\text{R}}$$

The pressure of the methane is

$$\begin{aligned} p_{\text{CH}_4} &= \frac{0.396(0.73)(920)}{8.518 - 0.684(0.396)} - \frac{578.9(0.396)^2}{(8.518)^2} \\ &= 32.25 - 1.25 \\ &= 31.0 \text{ atm} \end{aligned}$$

The pressure of the butane is

$$\begin{aligned} p_{\text{C}_4\text{H}_{10}} &= \frac{0.604(0.73)(920)}{8.518 - 1.944(0.604)} - \frac{3675(0.604)^2}{(8.518)^2} \\ &= 55.25 - 18.45 \\ &= 36.8 \text{ atm} \end{aligned}$$

Thus, the predicted pressure by Dalton's law is

$$\begin{aligned} p &= p_{\text{CH}_4} + p_{\text{C}_4\text{H}_{10}} \\ &= 31.0 + 36.8 = 67.8 \text{ atm} \quad \text{Ans} \end{aligned}$$

<sup>1</sup> Data are from REAMER, H. H., K. J. KORPI, B. H. SAGE, and W. N. LACEY, *Ind. Eng. Chem.*, **39** (No. 2), 206-209 (February, 1947).

The error from the true pressure of 68 atm is negligible. However, the perfect-gas equation of state predicts that

$$p = \frac{nR_0T}{v} = \frac{(1.0)(0.73)(920)}{8.518} = 78.8 \text{ atm}$$

$$\text{an error of } \frac{10.8}{68} = 0.159, \text{ or } 15.9 \text{ per cent}$$

*b Law of Additive Volume* Since van der Waals' equation is not explicit in volume, a trial-and-error method must be used, noting that here the pressure of the component is equal to the pressure of the mixture:

$$p = p_{\text{CH}_4} = p_{\text{C}_4\text{H}_{10}} = \frac{nR_0T}{V - bn} - \frac{an}{V^2}$$

$$V = V_{\text{CH}_4} + V_{\text{C}_4\text{H}_{10}}|_{p,T}$$

Equating van der Waals' equations for each component,

$$p = \frac{0.396(0.73)(920)}{V_{\text{CH}_4} - 0.2705} - \frac{578.9(0.396)^2}{V_{\text{CH}_4}^2} = \frac{0.604(0.73)(920)}{V_{\text{C}_4\text{H}_{10}} - 1.175} - \frac{3675(0.604)^2}{V_{\text{C}_4\text{H}_{10}}^2}$$

$$p = \frac{266}{V_{\text{CH}_4} - 0.2705} - \frac{90.7}{V_{\text{CH}_4}^2} = \frac{405}{V_{\text{C}_4\text{H}_{10}} - 1.175} - \frac{1,340}{V_{\text{C}_4\text{H}_{10}}^2}$$

Also, since the volume is known,

$$V = V_{\text{CH}_4} + V_{\text{C}_4\text{H}_{10}}|_{p,T} = 8.518 \text{ ft}^3$$

After several trial solutions,

$$V_{\text{CH}_4} = 4.464 \text{ ft}^3 \quad V_{\text{C}_4\text{H}_{10}} = 4.054 \text{ ft}^3$$

When either of these values is substituted in the appropriate van der Waals' equation, the pressure is calculated to be

$$p = 58.7 \text{ atm} \quad \text{Ans}$$

The error in this method of solution is

$$\frac{9.3}{68} = 0.136, \text{ or } 13.6 \text{ per cent}$$

In this instance the additive-pressure law is more exact than the additive-volume law. However, it should be remembered that van der Waals' equation is, also, a semiempirical relationship which will more precisely describe the state in some ranges than in others (Art 7-7). Thus, the combination of additive-volume and additive-pressure semiempirical laws with the semiempirical equation of state may well make the answer somewhat fortuitous. Notwithstanding, the method is to be preferred rather than to chance the perfect-gas equation.

*The Compressibility Factor for a Mixture.* The compressibility factor for a mixture can be found by substituting

$$p = \frac{ZnR_0T}{V} \quad \text{or} \quad V = \frac{ZnR_0T}{p} \quad (7-23)$$

in the additive-pressure or the additive-volume laws:

$$\begin{aligned} p &= p_a + p_b + \cdots \Big]_{T,v} \\ V &= V_a + V_b + \cdots \Big]_{p,T} \end{aligned}$$

For the additive-pressure law,

$$\begin{aligned} \frac{ZnR_0T}{V} &= \frac{Z_a n_a R_0T}{V} + \frac{Z_b n_b R_0T}{V} + \frac{Z_c n_c R_0T}{V} \Big]_{T,v} \\ nZ &= n_a Z_a + n_b Z_b + n_c Z_c \Big]_{T,v} \end{aligned} \quad (10-32a)$$

$$Z = x_a Z_a + x_b Z_b + x_c Z_c \Big]_{T,v} \quad (10-32b)$$

For the additive-volume law,

$$\begin{aligned} \frac{ZnR_0T}{p} &= \frac{Z_a n_a R_0T}{p} + \frac{Z_b n_b R_0T}{p} + \frac{Z_c n_c R_0T}{p} \Big]_{T,p} \\ nZ &= n_a Z_a + n_b Z_b + n_c Z_c \Big]_{T,p} \end{aligned} \quad (10-33a)$$

$$Z = x_a Z_a + x_b Z_b + x_c Z_c \Big]_{T,p} \quad (10-33b)$$

Although Eqs (10-32) and (10-33) have the same appearance, it should be noted that the conditions for evaluation are different, as indicated by the subscripts on the bracket.

**Example 20:** Calculate the pressure exerted by a mixture<sup>1</sup> of 0.396 mole methane and 0.604 mole butane if the volume is 8.518 ft<sup>3</sup> and the temperature is 460 F  
Ans 68 atm

**Solution** From Table VII (Appendix)

CH <sub>4</sub>	C <sub>4</sub> H <sub>10</sub>
$p_c = 45.8 \text{ atm}$	$p_c = 36.0 \text{ atm}$
$T_c = 343.3 \text{ R}$	$T_c = 766.8 \text{ R}$

*a Law of Additive Pressures* It will first be necessary to find the pseudo-reduced volume by

$$v_r' = \frac{p_c v}{R_0 T_c} = \frac{p_c (V/n_i)}{R_0 T_c} \quad (7-27c)$$

$$\text{CH}_4 \quad v_r' = \frac{45.8(8.518/0.396)}{0.73(343.3)} = 3.93$$

$$\text{C}_4\text{H}_{10} \quad v_r' = \frac{36.8(8.518/0.604)}{0.73(766.8)} = 0.908$$

Note that each component is evaluated at the mixture volume. The reduced temperature equals

<sup>1</sup> Data are same as for Example 19. See footnote, p. 345



$$\begin{array}{ll}
 & T_r = \frac{T}{T_c} \\
 \text{CH}_4 & T_r = \frac{920}{343.3} = 2.68 \\
 \text{C}_4\text{H}_{10} & T_r = \frac{920}{766.8} = 1.20
 \end{array}$$

The compressibility factors for the components at the volume and temperature of the mixture are found from Fig VII (Appendix)

$$\begin{array}{ll}
 \text{CH}_4 & \text{C}_4\text{H}_{10} \\
 T_r = 2.68 & v_r' = 3.93 & T_r = 1.20 & v_r' = 0.908 \\
 Z = 1.00 & & Z = 0.79 & \\
 (p_r = 0.7) & & (p_r = 1.05) &
 \end{array}$$

Substituting<sup>1</sup> these values for  $Z$  in Eq (10-32b),

$$\begin{aligned}
 Z &= (xZ)_{\text{CH}_4} + (xZ)_{\text{C}_4\text{H}_{10}} = 0.396(1.00) + 0.604(0.79) \\
 &= 0.87
 \end{aligned}$$

Then,

$$\begin{aligned}
 p &= \frac{ZR_0T}{v} = \frac{0.87(0.73)(920)}{8.518} \\
 &= 68.6 \text{ atm} \quad \text{Ans}
 \end{aligned} \tag{7-23}$$

The answer, in this instance, closely checks the experimental data

*b Law of Additive Volumes* The solution must be made by trial and error. From data in (a)

$$\begin{array}{ll}
 \text{CH}_4 & \text{C}_4\text{H}_{10} \\
 T_r = 2.68 & T_r = 1.20 \\
 p_r = \frac{p}{45.8} & p_r = \frac{p}{36.0}
 \end{array}$$

Also,

$$V_{\text{CH}_4} + V_{\text{C}_4\text{H}_{10}} = V = 8.518$$

and therefore

$$\left[ \frac{ZnR_0T}{p} \right]_{\text{CH}_4} + \left[ \frac{ZnR_0T}{p} \right]_{\text{C}_4\text{H}_{10}} = 8.518$$

$$Z_{\text{CH}_4}(0.396)(0.73)(920) + Z_{\text{C}_4\text{H}_{10}}(0.604)(0.73)(920) = 8.518p$$

$$266Z_{\text{CH}_4} + 405Z_{\text{C}_4\text{H}_{10}} = 8.518p$$

Arbitrarily select a value for  $p$ , then, find  $Z$  for each component from  $p_r$  and  $T_r$ . (Here the components are evaluated at the temperature and pressure of the mixture.) After a few trials

$$Z_{\text{CH}_4} = 1.01 \quad Z_{\text{C}_4\text{H}_{10}} = 0.64 \quad p = 62 \text{ atm} \quad \text{Ans.}$$

and this answer is

$$\frac{68 - 62}{68} = 0.088, \text{ or } 8.8 \text{ per cent too low}$$

<sup>1</sup> This procedure, rather than to use directly the reduced pressures read from the chart, will yield better accuracy

Kay<sup>1</sup> proposed that the pseudocritical temperature and pressure for the mixture could be found by the empirical equations:

$$T_{c'} = x_a T_{ca} + x_b T_{cb} + \quad (10-34a)$$

$$p_{c'} = x_a p_{ca} + x_b p_{cb} + \quad (10-34b)$$

**Example 21:** Repeat Example 20, using Kay's rules

**Solution:** For the data of Example 20

$$\begin{aligned} T_{c'} &= x_a T_{ca} + x_b T_{cb} \\ &= (0.396)(343.3) + (0.604)(766.8) = 599 \text{ R} \\ p_{c'} &= x_a p_{ca} + x_b p_{cb} \\ &= (0.396)(45.8) + (0.604)(36) = 39.85 \text{ atm} \end{aligned}$$

The reduced temperature is

$$T_{r'} = \frac{T}{T_{c'}} = \frac{920}{599} = 1.535$$

The pseudoreduced volume is obtained from

$$\begin{aligned} v_{r'} &= \frac{p_c v}{R_o T_{c'}} \quad (7-27c) \\ &= \frac{39.85(8.518)}{0.73(599)} \\ &= 0.776 \end{aligned}$$

With these values,  $Z$  is obtained from Fig. VII (Appendix)

$$Z = 0.87$$

and the pressure equals

$$p = \frac{ZR_o T}{v} = \frac{0.87(0.73)(920)}{8.518} = 68.5 \text{ atm} \quad Ans$$

(Compare with the experimental value of 68 atm.)

### Problems

Standard barometric pressure of 14.696 psia is used unless otherwise specified

1. A mixture of 5 lb<sub>m</sub> of argon, 10 lb<sub>m</sub> of nitrogen, and 10 lb<sub>m</sub> of methane has a pressure of 20 psia and a temperature of 100 F. Determine for the mixture (a) the molecular weight, (b) the partial pressure and partial volumes, and (c) the molar volume (volume of 1 mole of mixture)

2. Repeat Prob. 1, but assume that the mixture consists of 2 moles of oxygen and 3 moles of hydrogen

3. A mixture, containing 26 lb<sub>m</sub> of nitrogen and the remainder oxygen, occupies a volume of 100 ft<sup>3</sup> at a pressure of 75 psia and temperature of 60 F. Determine the molecular weight of the mixture and the partial pressure of the nitrogen

4. Repeat Prob. 3 but assume that the mixture contains 0.3 mole fraction of nitrogen and 0.7 mole fraction of oxygen.

<sup>1</sup> Kay, W. B., Density of Hydrocarbon Gases and Vapors, *Ind. Eng. Chem.*, **28** (No. 9), 1014-1019 (September, 1936)

5. A mixture of 0.1 mole of oxygen and the remainder carbon dioxide occupies a volume of 100 ft<sup>3</sup> at a pressure of 200 psig. If the partial pressure of the carbon dioxide is 150 psia, what is the temperature of the gas?

6. Derive the relationship  $mR = m_a R_a + m_b R_b + m_c R_c$ .

7. Determine the volumetric analysis for the data of Probs 1 through 6.

8. Determine the gravimetric and ultimate analysis for the data of Probs 1 through 6.

9. A mixture of 30 per cent nitrogen and 70 per cent carbon dioxide (by volume) has a temperature of 200 F. Calculate the internal energy and enthalpy of this mixture above a datum of 0 F for the internal energy (use variable-heat-capacity relationships) on a mole and also a pound-mass basis.

10. Repeat Prob 9 but for a temperature of 600 F.

11. Ten pounds mass oxygen at 100 psia and 200 F is in a container that is connected through a valve to a second container filled with 20 lb<sub>m</sub> carbon dioxide at 50 psia and 100 F. The valve is opened, and adiabatic mixing occurs. Determine the final pressure and temperature.

12. Repeat Prob 11, but assume that the second tank contained 0.5 mole of nitrogen.

13. Repeat Prob 11, assuming that the process was not adiabatic and that 10 Btu of heat was transferred to the surroundings during (and not after) the mixing process. (Use constant values for the heat capacities.)

14. Determine the probable volumetric analysis for the data of Prob 11.

15. Compute the change in entropy for the data of Prob 11.

16. Compute the change in entropy for the data of Prob 12.

17. Compute the change in entropy and enthalpy for the data of Prob 13.

18. A mixture containing 0.3 mole fraction of air and 0.7 mole fraction of methane is compressed from  $p_1 = 14.7$  psia and  $t_1 = 60$  F to  $p_2 = 120$  psia. Compute the final temperature of the mixture and the change in entropy for each component. (Use constant values for the heat capacities.)

19. Repeat Prob 18, using variable-heat-capacity relationships.

20. Repeat Prob 18, assuming that the final state has a volume one-sixth of the original volume (and  $p_2$  is unknown).

21. A mole of air saturated with water vapor is in a tank at a temperature of 300 F and a pressure of 100 psia. Determine the amount of water vapor in the mixture.

22. If the mixture in Prob 21 is cooled to 200 F, what will be the pressure? How much heat must be transferred in this process? (Use constant value of heat capacity for the air and Steam Table values for the water.)

23. Compute the change in entropy for the data of Prob 21. (Use Steam Table data for the water.)

24. Repeat Example 9, assuming that the temperature in the manifold is 50 F and the vapor pressure is 0.45 psia.

25. What must be the pressure in the manifold of the engine in Example 9 if the air mixture is saturated? (Temperature is 60 F.)

26. A mixture of 0.2 lb<sub>m</sub> steam and 0.2 lb<sub>m</sub> air is in a tank at a temperature of 200 F. Determine the volume and the pressure in the tank.

27. Determine the heat that must be transferred to raise the temperature of the mixture in Prob 26 to 300 F.

28. The temperature in a room is 68 F and the specific humidity is 0.006.

Calculate the relative humidity and the density of each component, and find the dew point.

**29.** Determine how much moisture must be added or removed from 1,000 cfm of the air in Prob 28 to change the temperature to 80 F and the relative humidity to 50 per cent

**30** Calculate the heat that must be transferred during the process of Prob 29

**31.** Air has a dry-bulb temperature of 60 F and a wet-bulb temperature of 50 F Calculate the relative humidity, humidity ratio, the dew point, and the density of the mixture

**32** Air has a dry-bulb temperature of 75 F and a relative humidity of 50 per cent Determine the temperature of adiabatic saturation, the humidity ratio, the dew point, and the enthalpy of the mixture

**33.** Check Probs 31 and 32 by means of the psychrometric chart

**34** A stream of 1,000 cfm of saturated air at 60 F is mixed with 1,500 cfm of recirculated air at 75 F and 60 per cent Determine the final condition of the mixture

**35.** Air at 60 F and 30 per cent relative humidity is to be added to 1,000 cfm air at 80 F and 60 per cent relative humidity to achieve a resultant mixture at 70 F Determine the amount of air that must be added and the final conditions of the mixture

**36.** A stream of 1,000 cfm of air at 90 F and 90 grains specific humidity is to be cooled to 75 F using a cooling coil with surface temperature above the dew point of the air How much heat must be transferred?

**37.** The air in Prob 36 is to be cooled and dehumidified by using a coil with a mean surface temperature of 50 F If the resultant air stream after mixing and cooling has a relative humidity of 90 per cent, compute the amount of heat that was removed

**38** Air at 85 F and 50 per cent relative humidity is to be cooled and dehumidified by a coil with mean surface temperature of 50 F If the performance factor of the coil,

$$\frac{t_{\text{air in}} - t_{\text{air out}}}{t_{\text{air in}} - t_{\text{coil}}}$$

is 0.90, determine the final conditions of the air and the amount of heat transferred

**39** Air at 50 F,  $\phi = 40$  per cent, is to be conditioned to 72 F and  $\phi = 50$  per cent, in the following processes (a) heating at constant humidity ratio, (b) humidified at constant wet-bulb temperature (to saturation), (c) heating at constant humidity ratio Determine the condition of the air after each process and the heat transferred during each process

**40** Repeat Prob 39, assuming that the air temperature in the evaporative cooling process is reduced by 80 per cent of the original wet-bulb depression

**41.** Water at 120 F enters a cooling tower and leaves at 77 F Air enters the tower at 80 F and 30 per cent relative humidity and leaves at 110 F Determine the air flow necessary to furnish 100,000 lb<sub>m</sub> hr<sup>-1</sup> of cooled water and the water make-up rate

**42.** Discuss the term *saturated* as applied to a liquid, vapor, and mixture.

**43.** Show that the difference in datum states between the air and the water steam in the empirical equations in Example 13 does not affect the validity of the final equation

44. Determine the approximations made in deriving Eq (10-25) [Substitute Eq (10-19) and  $\Delta h = 0.24(t_2 - t_1)$  in Eq (10-24), and then note simplifications necessary to obtain Eq (10-25) ]

45. Calculate the pressure exerted by a mixture of 0.5 mole of methane and 0.5 mole of propane if the temperature is 194 F and the volume is 7.65 ft<sup>3</sup>. Use van der Waals' equation and the law of additive pressures. (Observed pressure is 50 atm.)

46. Repeat Prob 45, using the law of additive volumes.

47. Repeat Probs 45 and 46, using the compressibility factors. (Note that the propane is in the liquid state for the conditions of Amagat's law,  $Z$  is estimated from the chart to be 0.2.)

48. Repeat Prob 45, using Kay's rules.

In Probs 49 through 52 calculate the molar volume of a mixture of 0.1879 mole fraction of methane and 0.8121 mole fraction of butane if the pressure is 4,000 psia and the temperature is 100 F. (Observed volume is 1.4363 ft<sup>3</sup>.)

49. By van der Waals' equation and the law of additive pressures.

50. By using van der Waals' equation and the law of additive volumes.

51. Using compressibility factors.

52. Using Kay's rules.

### Symbols

$a, b$	van der Waals' constants
$c$	heat capacity
F	Fahrenheit temperature scale
$h$	specific enthalpy
$H$	enthalpy, most often, of 1 lb <sub>m</sub> air plus $\omega$ lb <sub>m</sub> water vapor
$k$	ratio of $c_p/c_v$
$M$	molecular weight
$m$	mass, also, mass flow rate
$n$	mole
$p$	pressure
psia	absolute pressure (lb <sub>f</sub> /in. <sup>2</sup> )
psig	gauge pressure (lb <sub>f</sub> /in. <sup>2</sup> )
$Q$	heat, also, heat rate
$R$	specific gas constant
$R_0$	universal gas constant
R	Rankine temperature scale
$s$	specific entropy
$S$	entropy
$t$	temperature, thermodynamic
$T$	absolute temperature
$u$	specific internal energy
$U$	internal energy
$v$	specific volume
$V$	volume
$W$	work
$x$	mole fraction
$Z$	compressibility factor
$\approx$ or $\rightarrow$	approaches equality

**Greek Letters**

$\phi$	(phi)	relative humidity
$\Sigma$	(sigma)	summation
$\rho$	(rho)	density
$\omega$	(omega)	humidity ratio—specific humidity

**Subscripts**

$a, b, c, i$	components of mixture
$a$	air
$c$	critical state
$f$	liquid water (subcooled or saturated)
$fg$	change from saturated liquid to saturated vapor
$g$	saturated-vapor value in Steam Table
$m$	mass
mix	mixture
$N$	nitrogen
$O$	oxygen
$p$	constant pressure
$r$	reduced property
$r$	pseudoreduced property
$s$	saturated vapor
$v$	constant volume
$w$	water vapor (steam)

**Superscript**

*	state of adiabatic saturation
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**Suggested Reference**

- 1 "Heating, Ventilating, Air Conditioning Guide," American Society of Heating and Ventilating Engineers, New York, 1946









## CHAPTER XI

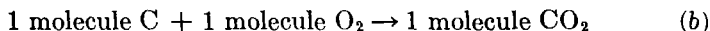
### THERMOCHEMICAL CALCULATIONS

The chemistry of the combustion process is an engineering problem of practical and, also, theoretical significance. The practicing engineer must be able to calculate an energy balance for the commercial power system, and he should be aware of the limitations to the process of combustion that theory is able to predict.

**11-1. Combustion Equations.** Consider the reaction taking place when carbon unites with oxygen to form carbon dioxide



This equation can be read 1 molecule of carbon unites with 1 molecule of oxygen to form 1 molecule of carbon dioxide.



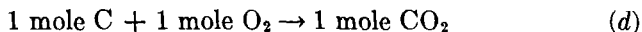
The relative masses of these molecules are shown by the molecular weights

$$\text{C} = 12 \quad \text{O}_2 = 32 \quad \text{CO}_2 = 44$$

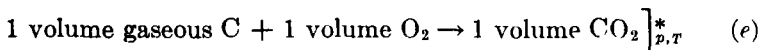
and, therefore,

$$\begin{aligned} 12 \text{ units mass C} + 32 \text{ units mass O}_2 &= 44 \text{ units mass CO}_2 \\ 12 \text{ lb}_m \text{ C} + 32 \text{ lb}_m \text{ O}_2 &= 44 \text{ lb}_m \text{ CO}_2 \end{aligned} \quad (c)$$

In this manner the chemical-reaction equation is converted into a mass equation. Each mass shown in Eq (c) is, by definition, a mole (Art 7-5), and therefore Eq (a) is equivalent to



A mole of any perfect gas, under fixed conditions of temperature and pressure, occupies a definite volume, and this condition is approximated by real gases at low pressures. Thus, Eq (d) can be written

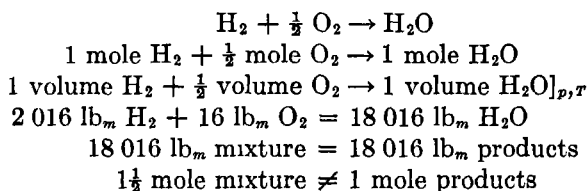


Comparison of Eqs (a), (b), (d), and (e) shows that Eq (a) can be

\* The subscripts on the bracket indicate that all volumes must be evaluated at the same pressure and temperature

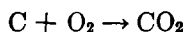
interpreted to be either a molecular, a molar, or, with some approximation, a volumetric equation. This basic form of the chemical equation can always be converted into a mass equation by multiplying each term by the appropriate molecular weight (Eq. c).

By the same line of reasoning, the equation for the combustion (or reaction) of hydrogen and oxygen can be written in any of the following forms .

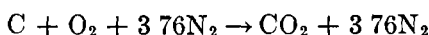


These equations show that the mass of mixture must equal the mass of products, although the number of moles (and volumes) of mixture and products are not necessarily equal.

In most instances, the combustion process is with atmospheric air and not with pure oxygen. The nitrogen and other gases in the air merely dilute the concentration of oxygen and usually appear in the products unchanged in form. For example, the combustion of carbon and pure oxygen is



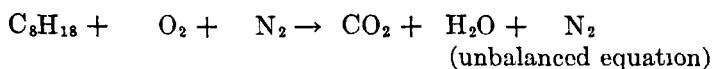
and when the oxygen is supplied by dry air, 3.76 moles of nitrogen and other inert gases will accompany each mole of oxygen



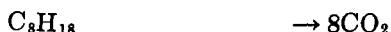
Here the symbol  $\text{N}_2$  includes all of the inert gases found in atmospheric air. When the molecular weight of 28.161 (Art. 10-8) is assigned to these gases, the mass equation is determined.



The steps in balancing the chemical equation can be illustrated by the complete combustion of octane ( $\text{C}_8\text{H}_{18}$ ) with the *theoretical* amount of dry air



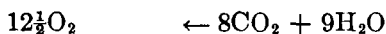
First, a carbon balance is made ( $C_{\text{mixture}} = C_{\text{products}}$ )



then, a hydrogen balance ( $H_{\text{mixture}} = H_{\text{products}}$ )



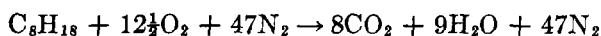
followed by an oxygen balance ( $O_{\text{products}} = O_{\text{mixture}}$ )



and, finally, a nitrogen balance ( $\text{N}_2 = 3.76 \text{ O}_2$ )



The complete combustion equation is



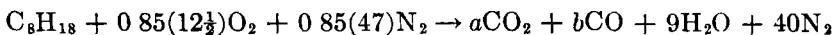
The relative masses of air and fuel taking part in the reaction is of interest. The *air-fuel ratio* is defined as a mass ratio

$$AF = \frac{\text{mass air}}{\text{mass fuel}} = \frac{12\frac{1}{2}(32) + 47(28.16)}{8(12) + 18(1.008)} = 15.1 \text{ to } 1 \left( \text{or } \frac{15.1 \text{ lb}_m \text{ air}}{\text{lb}_m \text{ fuel}} \right)$$

The usual case of combustion involves a quantity of air either insufficient for complete combustion or else in excess. Assume that 25 per cent *excess air*, instead of the theoretical amount, is supplied to the reaction of  $\text{C}_8\text{H}_{18}$  and air:



The excess air appears in the products unchanged in form. When insufficient air is supplied, not all the carbon will be oxidized to carbon dioxide, and free hydrogen may appear. Assume that the products of combustion are carbon dioxide, carbon monoxide, water vapor, and nitrogen (neglecting hydrogen) when octane is burned with 85 per cent of the theoretical amount of dry air



A carbon balance

$$8 = a + b$$

An oxygen balance

$$10.62 = a + \frac{b}{2} + \frac{9}{2}$$

When these two equations are solved simultaneously,

$$a = 4.25$$

$$b = 3.75$$

and the balanced-reaction equation is



**11-2. Combustible Elements in Fuel.** The combustible elements in fuels are predominantly carbon and hydrogen with small amounts of sulphur as the only other essential fuel element. Solid fuels, such as coal, consist of carbon, hydrogen, and oxygen with other elements appearing in small amounts. A representative ultimate analysis of a dry bituminous coal, exclusive of ash and moisture, might appear: C, 88; H, 6, 0, 4; N, 1, and S, 1. Liquid fuels are mixtures of complex hydrocarbons, although for combustion calculations gasoline or fuel oil can be assumed to average<sup>1</sup> the molecular formula  $\text{C}_8\text{H}_{17}$ . The same procedure cannot be used for coals because analyses of different coals vary widely.

**Example 1:** What would be an equivalent formula for a hydrocarbon fuel that analyzes 87 per cent C and 12 per cent H?

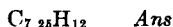
**Solution:** The formula will be of the form



and by the analysis and molecular weights

$$\begin{aligned} (12)a &= 87 & \text{or} & & a &= 7.25 \\ (1)b &= 12 & \text{or} & & b &= 12 \end{aligned}$$

The result is



If desired, this answer can be multiplied by 4 to obtain whole numbers:



**Example 2:** Determine the complete-combustion equation for the representative coal analysis listed in this article.

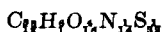
**Solution:** The formula for the coal can be represented by



The ultimate analysis is

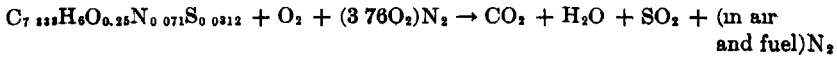
C	H	O	N	S
88%	6%	4%	1%	1%

The formula is equivalent to



and a "mole" of this coal will have a mass of 100 lb<sub>m</sub>. The reaction equation for this artificial mole unit is

<sup>1</sup> This value is probably more exact for mid-continent gasolines than a value obtained from a single ultimate analysis.



As before, a carbon balance:

$$7.333\text{C} \rightarrow 7.333\text{CO}_2$$

A hydrogen balance

$$6\text{H} \rightarrow 3\text{H}_2\text{O}$$

A sulphur balance

$$0.0312\text{S} \rightarrow 0.0312\text{SO}_2$$

An oxygen balance

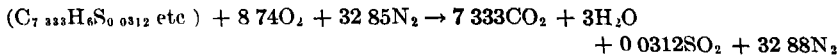
$$\frac{0.25}{2} + \text{O}_2 \leftarrow 7.333 + \frac{3}{2} + 0.0312$$

$$\text{or} \quad \text{O}_2 = 8.74 \text{ (oxygen supplied by air)}$$

Finally, a nitrogen balance

$$\begin{aligned} \text{N}_2 &= \frac{0.071}{2} (\text{fuel}) + 3.76(8.74)(\text{air}) \\ &= 0.035 + 32.85 \\ &= 32.88 (\text{nitrogen in products}) \end{aligned}$$

The complete equation for 1 "mole" (100 lb<sub>m</sub>) of dry and ash-free coal is



Note that the oxygen, hydrogen, and sulphur in the fuel could have been neglected for simplicity without significantly affecting the accuracy of the solution

**Example 3** Compute the air-fuel ratio for the data of Example 2.

**Solution:** The mass of air is computed, the molecular weight of air being noted as closely 29

$$\text{Mass air} = 29(8.74 + 32.85) = 1,207 \text{ lb}_m \text{ air}$$

Since the artificial mole unit was set up from an ultimate analysis that totaled 100 units, then 1 mole of coal has a mass of 100 lb, and the air-fuel ratio is

$$A/F = \frac{\text{mass air}}{\text{mass fuel}} = \frac{1,207}{100} = 12.07 \frac{\text{lb}_m \text{ air}}{\text{lb}_m \text{ fuel}} \quad \text{Ans}$$

However, this is for ash and moisture-free coal. Suppose the coal as fired had 8 per cent water and 10 per cent ash, then

$$\begin{aligned} \frac{a \text{ lb}_m \text{ water} \times 100}{(100 \text{ lb}_m \text{ dry ash-free coal}) + a + b} &= 8 \text{ per cent} \\ \frac{b \text{ lb}_m \text{ ash} \times 100}{(100 + a + b)} &= 10 \text{ per cent} \end{aligned}$$

Solving these equations,

$$\begin{aligned} a &= 9.75 \text{ lb}_m \text{ H}_2\text{O}/100 \text{ lb}_m \text{ dry ash-free coal} \\ b &= 12.19 \text{ lb}_m \text{ ash}/100 \text{ lb}_m \text{ dry ash-free coal} \\ &\quad \underline{21.94} \end{aligned}$$

Then, the gross amount of coal burned is not 100 lb<sub>m</sub> but 121.94 lb<sub>m</sub>, and the air-fuel ratio equals

$$AF = \frac{\text{mass air}}{\text{mass fuel}} = \frac{1207}{121.94} = 9.9 \frac{\text{lb}_m \text{ air}}{\text{lb}_m \text{ fuel as fired}} \quad \text{Ans}$$

**Example 4:** (a) Compute the mass of dry flue gas per pound of coal for the data of Examples 2 and 3. (b) If the flue gases leave at 640 F and the atmospheric temperature is 77 F, determine the energy carried away in the hot gases per pound of coal.

**Solution:**

a The water vapor formed in the combustion of the hydrogen is assumed to be condensed. The gases remaining are

$$\begin{array}{rcl} \text{Mass of CO}_2 & 7.333(44) & = 322.3 \text{ lb}_m \\ \text{Mass of SO}_2 & 0.0312(64) & = 2.0 \text{ lb}_m \\ \text{Mass of N}_2 & 32.88(28.16) & = 926.0 \text{ lb}_m \\ & & \hline & & 1,250.3 \text{ lb}_m/\text{mole of coal} \end{array}$$

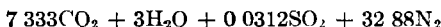
As before, these products can be divided by the mass of fuel, 100 lb<sub>m</sub>.

$$12.50 \frac{\text{lb}_m \text{ dry flue gas}}{\text{lb}_m \text{ fuel (ash and moisture free)}} \quad \text{Ans}$$

Or on the basis of coal as fired

$$\frac{1,250.3}{121.94} = 10.24 \frac{\text{lb}_m \text{ dry flue gas}}{\text{lb}_m \text{ fuel as fired}}$$

b The flue gases are



These gases leave the furnace at 640 F. But the gases should have been cooled to the atmospheric temperature of 77 F, and then *sensible heat* could have been transferred to a thermodynamic cycle. (*Sensible heat* is the name assigned to heat obtained through change in temperature but without change in phase or composition of the mass.) Thus, the hot gases, by virtue of their high temperature, represent a loss of sensible heat. Since the pressure is constant, the sensible-heat loss is evaluated by the enthalpy difference of the gases between 640 and 77 F [Eq. (4-4)]. Table XI (Appendix) is one means for evaluating the enthalpy difference. For CO<sub>2</sub>,

$$1100 \text{ R} \quad \frac{h}{T} = 8.9138 \text{ Btu/mole R} \quad \text{and} \quad h_{1100 \text{ R}} = 9805.2 \text{ Btu/mole}$$

$$537 \text{ R} \quad \frac{h}{T} = 7.5064 \quad \text{and} \quad h_{537 \text{ R}} = 4028.6 \text{ Btu/mole}$$

Therefore,

$$\Delta h \Big|_{537 \text{ R}}^{1100 \text{ R}} = 5776.6 \text{ Btu/mole}$$

Let the moles of SO<sub>2</sub> and CO<sub>2</sub> be combined because of the small quantity of SO<sub>2</sub> present. The sensible-heat loss equals

$$\Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = (\text{moles CO}_2 + \text{SO}_2)(\Delta h) = 7.364(5776.6) = 42,538.9 \text{ Btu}$$

In similar fashion, the heat losses are found for the  $\text{H}_2\text{O}$  and  $\text{N}_2$

$$\begin{array}{ll} 3 \text{ moles } \text{H}_2\text{O} & \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 14,064.3 \text{ Btu} \\ 32.88 \text{ moles } \text{N}_2 & \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 130,565.5 \text{ Btu} \end{array}$$

The total heat loss is the sum of the enthalpy differences

$$\Sigma \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 187,168.7 \text{ Btu/mole coal as fired} \quad \text{Ans}$$

Since there are 121.94 lb<sub>m</sub> coal as fired per mole,

$$\frac{187,168.7}{121.94} = 1533 \text{ Btu/lb}_m \text{ coal as fired} \quad \text{Ans}$$

Solutions can also be found by the data in Table X (Appendix) (or Table IIC) For  $\text{CO}_2$ ,

$$\begin{array}{ll} 1100 \text{ R } u + \frac{pv}{J} & = 4778 + 2185 = 6963 \text{ Btu/mole} \\ 537 \text{ R } u + \frac{pv}{J} & = 118 + 1068 = 1186 \text{ Btu/mole} \\ \cdot & \Delta h \Big|_{537 \text{ R}}^{1100 \text{ R}} = 5777 \text{ Btu/mole} \\ 7.364 \text{ moles } (\text{CO}_2 + \text{SO}_2) & \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 42,536 \text{ Btu} \end{array}$$

In similar fashion for the  $\text{H}_2\text{O}$  and  $\text{N}_2$

$$\begin{array}{ll} 3 \text{ moles } \text{H}_2\text{O} & \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 14,037 \text{ Btu} \\ 32.88 \text{ moles } \text{N}_2 & \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} = 130,501 \text{ Btu} \\ \Sigma \Delta H \Big|_{537 \text{ R}}^{1100 \text{ R}} & = 187,074 \text{ Btu/mole of coal as fired} \end{array}$$

Comparison shows that the two answers, one from the data of Table XI (Appendix), and the other from the data of Table X (Appendix), check quite closely

A more exact solution can be made by including the humidity of the air (used for combustion of the coal) in the calculations

**11-3. Analysis of the Products of Combustion.** The usual laboratory equipment for analyzing gas mixtures is the Orsat apparatus, a portable model is illustrated in Fig 11-1. The Orsat consists of a measuring burette *a* (which contains 100 units of volume between the zero mark on the scale and the upper hairline at *b*) and a series of absorption pipettes such as *c*, *d*, and *e*. This particular model is for mixtures containing carbon dioxide, oxygen, or carbon monoxide, although additional pipettes for other gases can also be added. The method of making a test can be summarized as follows. A sample of gas is drawn through valve *f* into burette *a* by lowering the leveling



bottle *g*, which contains a liquid, usually water. Valve *f* is then closed, and valve *h* is opened to the atmosphere. Surplus gas is expelled by raising the leveling bottle until the level in *g* coincides with the zero mark. This procedure ensures that the sample of 100 units of volume is at atmospheric pressure, while the thermal capacity of the apparatus ensures that the temperature of the sample is also

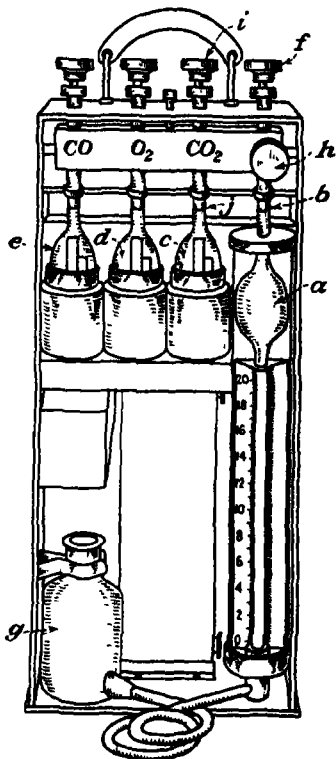


FIG 11-1 Ellison Orsat for determining  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CO}$

atmospheric. Now by opening valve *i* and raising the leveling bottle, the gas in the measuring burette is forced into pipette *c*. Pipette *c* contains a solution of potassium hydroxide that will absorb carbon dioxide. Next, the leveling bottle is lowered and the sample is returned to the measuring burette, while the level of the solution in the pipette returns to the index point *j*. When the leveling bottle is held with the water levels in *g* and *a* equal, the pressure of the sample is restored to the initial pressure (atmospheric) (while the temperature remains constant at the initial value). Thus, the reading made at this point represents the volume of carbon dioxide, measured at atmospheric temperature and pressure, that was absorbed in the first pipette. This volume is the partial volume of the carbon dioxide in the original dry mixture. The procedure is repeated by passing the gas into the second pipette, which contains a solution of pyrogallie acid. Here the oxygen is absorbed, and the remainder of the gas is returned

to the measuring burette. The volume that is now measured is less than the original 100 units by an amount equal to the partial volumes of the  $\text{CO}_2$  and the  $\text{O}_2$  in the original dry mixture. The partial volume of the oxygen is readily calculated since the partial volume of the  $\text{CO}_2$  is known. (In similar manner the third pipette containing cuprous chloride absorbs carbon monoxide that may be present.)

In all Orsat instruments, the analysis is determined volumetrically and appears on a dry basis, although the original sample was saturated

with water vapor. This is because the absorption processes occur at constant temperature and therefore the partial pressure of the water vapor remains constant. By Eq (10-7)

$$p_s = \frac{n_s}{n_{\text{mixture}}} \times 14.7 \text{ psia}$$

Since  $n_{\text{mixture}}$  is progressively decreasing as each component is removed from the mixture,  $n_s$  must also progressively decrease if the partial pressure is to remain constant. Thus, whenever a gas is absorbed in one of the pipettes, a proportional amount of water vapor is also condensed, and therefore the Orsat analysis is not the true analysis of the mixture. As shown in Example 5, the Orsat merely ignores the water vapor and reports the exact analysis for a hypothetical dry mixture.

**Example 5:** Show that an Orsat measures the dry percentages of the mixture.

**Solution:** Assume that the initial saturated mixture contains 10 per cent  $\text{CO}_2$ , 2 per cent  $\text{H}_2\text{O}$  (saturated vapor), and 88 per cent  $\text{N}_2$ . Since the temperature remains constant,

$$p_s = \frac{n_s}{n} \times 14.7 = \text{constant} \quad (10-7)$$

Therefore,

$$x_s = \frac{n_s}{n} = \text{constant}$$

The mole fraction of water vapor in the original mixture is

$$x_s = \frac{n_s}{n} = \frac{2}{100} = 0.02$$

After the  $\text{CO}_2$  has been absorbed, the mole fraction of water vapor must still equal 0.02

$$x_s = 0.02 = \frac{2 - \text{condensed } \text{H}_2\text{O}}{90 - \text{condensed } \text{H}_2\text{O}}$$

Condensed  $\text{H}_2\text{O}$  = 0.204 per cent

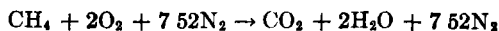
This calculation shows that the contraction of the mixture when the  $\text{CO}_2$  is removed is not 10 units but 10.204 units. But 10.204 is the dry percentage of  $\text{CO}_2$  in the original mixture.

$$\text{CO}_2 = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2} + n_{\text{N}_2}} \times 100 = \frac{10}{98} \times 100 = 10.204 \text{ per cent}$$

Thus, the Orsat measures the exact percentage of carbon dioxide in the dry mixture and not the actual percentage in the real mixture.

**Example 6:** Determine the dew point for the products of combustion of methane and air at atmospheric pressure.

**Solution:**



$$\text{Partial pressure of } \text{H}_2\text{O} = \frac{2 \text{ moles } \text{H}_2\text{O}}{10.52 \text{ moles product}} \times 14.7 = 2.8 \text{ psia}$$

The Steam Tables show that this pressure corresponds to a saturation temperature of 139 F, which is the dew point *Ans*

**Example 7:** What will be the components of the mixture of Example 6 in an Orsat at 70 F?

**Solution:** When the mixture is cooled to 70 F, a part of the water vapor will condense. The partial pressure of the water vapor at 70 F can be found from the Steam Tables  $p_s = 0.363$  psia and

$$p_s = \frac{\text{moles H}_2\text{O}}{\text{moles products}} \times 14.7 = \frac{x}{1 + 7.52 + x} \times 14.7 = 0.363 \text{ psia}$$

Solving this gives

$$x = 0.26 \text{ mole}$$

The products in the Orsat are



**Example 8.** For the data of Example 7 what will be the percentage of  $\text{CO}_2$  in the wet and the dry products?

**Solution:** The percentage of  $\text{CO}_2$  on a wet basis is

$$\text{CO}_2 = \frac{1 \text{ mole CO}_2}{8.78 \text{ mole products}} \times 100 = 11.4 \text{ per cent} \quad \text{Ans}$$

The percentage of  $\text{CO}_2$  on a dry basis is

$$\text{CO}_2 = \frac{1 \text{ mole CO}_2}{8.52 \text{ mole products}} \times 100 = 11.72 \text{ per cent} \quad \text{Ans}$$

The latter value would be the percentage reported by the Orsat analysis

**11-4. The Reaction Equation and the Orsat Analysis.** In industry, the engineer is called upon to make heat balances or related calculations that depend on the interrelationships between the masses of air and fuel. In many instances, measurement of air quantities is a difficult task, and indirect methods must be used. The different techniques that are available for approximate solutions of the problems that may be met are illustrated in the following examples. In most, if not all, instances the amount of water vapor present in the real mixture cannot be directly measured.

The procedures to be followed can be subdivided into the following groups:

*a Exact Analysis of the Fuel and Exact Analysis of the Products of Combustion Are Known* This is the preferable case, and either a carbon or an oxygen-hydrogen balance can be used, both methods should give the same answer if the analyses are correct. However, when the fuel is predominantly carbon—coal, for example—the oxygen-hydrogen balance is more liable to error because of the small quantities that are measured in the analyses. Correspondingly, the presence of smoke

signifying incomplete combustion may make the carbon balance incorrect

*b Exact Analysis of the Fuel and Incomplete Analysis of the Products of Combustion Are Known.* In many instances carbon dioxide, oxygen, and carbon monoxide are the only products that are measured. When coal is the fuel, the balance of the dry products can be assumed to be "nitrogen" with molecular weight of 28.161. When hydrocarbon fuels are used and the mixture does not contain too great an excess of air, empirical rules can be used:

$$\begin{aligned}\text{Percentage H}_2 &= \frac{1}{2} \text{ per cent CO} \\ \text{Percentage CH}_4 &= 0.3 \text{ per cent (constant)}\end{aligned}$$

Traces of methane are invariably found in the products of combustion of hydrocarbon fuels, and a constant percentage can be assumed to be present.

The carbon balance is preferred for cases under this grouping.

*c Analysis of the Fuel Is Unknown.* Here a carbon-hydrogen balance must be made unless the composition of the fuel can be approximated. Most gasolines and fuel oils sold in the Central and Eastern states can be closely represented by the molecular formula<sup>1</sup>  $\text{C}_8\text{H}_{17}$ . With this approximation, either the carbon or oxygen-hydrogen balance can be used depending on the presence of factors noted under headings (a) and (b) above.

**Example 9.** (*Carbon balance method when ultimate analysis of the fuel is known*)  
An anthracite coal has the following ultimate analysis:

C	H	O	N	H <sub>2</sub> O	Ash	Total
70%	3%	3%	1%	11%	12%	100% (gravimetric)

The Orsat analysis of the flue gas is

CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	Total
14.6%	0.2%	5.5%	79.7%	100% (volumetric)

Determine the mass of dry air required per pound of fuel if the cinder in the ashpit is 40 per cent carbon.

<sup>1</sup> When the fuel contains a known percentage of aromatics, the formula can be adjusted by considering the aromatics to be 92 per cent C and 8 per cent H (by mass).

**Solution:** In the same manner as in Example 2, the coal can be assigned a molecular formula. However, for acceptable accuracy, only the carbon need be treated

$$[C_{83}HON(H_2O)(Ash)] = 100 \text{ lb}_m \text{ of coal as fired}$$

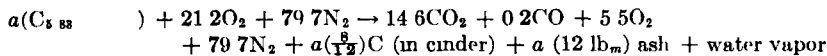
Since 60 per cent of the cinder is ash and 40 per cent is carbon, the mass of cinder per 100 lb<sub>m</sub> of coal must be 20 lb<sub>m</sub>.

$$\begin{aligned} x(0.60) &= 12 \text{ lb}_m \text{ ash in 100 lb}_m \text{ coal} \\ x &= 20 \text{ lb}_m \text{ cinder/100 lb}_m \text{ coal as fired} \end{aligned}$$

and the carbon in cinder equals

$$C = 0.40(20) = 8 \text{ lb}_m \text{ C/100 lb}_m \text{ coal as fired}$$

With these values the complete reaction equation can be written (although inconsistent units are shown)



Here a nitrogen balance has been made, assuming that the nitrogen in the coal was of negligible amount, and,

$$O_2 = \frac{N_2}{3.76} = \frac{79.7}{3.76} = 21.2$$

A carbon balance for  $a$

$$\begin{aligned} 5.83a &= 14.6 + 0.2 + 0.75a \\ a &= 2.92 \end{aligned}$$

and the air-fuel ratio is

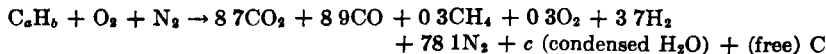
$$AF = \frac{\text{mass air}}{\text{mass fuel}} = \frac{(21.2 + 79.7)29}{2.92 \times 100} = 10.01 \frac{\text{lb}_m \text{ air}}{\text{lb}_m \text{ fuel as fired}} \quad \text{Ans}$$

**Example 10:** (Hydrogen-balance method when ultimate analysis of the fuel is known) A hydrocarbon with formula  $C_8H_{17}$  is burned with dry air, and the products of combustion are as follows:

CO <sub>2</sub>	CO	CH <sub>4</sub>	O <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	C
8.7%	8.9%	0.3%	0.3%	3.7%	78.1%	free carbon (smoke)

Determine the air-fuel ratio

**Solution:** Since free carbon is present in the products of combustion, a hydrogen balance should give the best results



The nitrogen in the mixture equals that in the products, while the oxygen is equal to

$$O_2 = \frac{N_2}{3.76} = \frac{78.1}{3.76} = 20.8$$

An oxygen balance is made to find the amount of water vapor:

$$20.8O_2 = 8.7 + \frac{8.9}{2} + 0.3 + \frac{c}{2}$$

$$c = 14.7$$

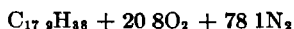
A hydrogen balance is then made:

$$b = 0.3(4) + 3.7(2) + 14.7(2) = 38$$

The ratio of  $b$  to  $a$  for the fuel  $C_8H_{17}$  is 2.12, hence,

$$\frac{b}{a} = 2.12 \quad a = \frac{38}{2.12} = 17.9$$

Therefore, the mixture is

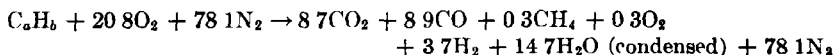


and the air-fuel ratio is

$$AF = \frac{\text{mass of air}}{\text{mass of fuel}} = \frac{(98.9)(29)}{(17.9)(12) + 38(1)} = 11.3 \frac{\text{lb}_m \text{ air}}{\text{lb}_m \text{ fuel}} \quad \text{Ans}$$

**Example 11:** (*Carbon-hydrogen balance when composition of fuel is unknown and cannot be approximated*) Assume that the fuel in Example 10 is of unknown composition and that the products of combustion do not contain free carbon

**Solution:** The reaction is set up as before



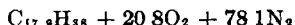
A carbon balance for  $a$

$$a = 8.7 + 8.9 + 0.3 \\ = 17.9$$

An oxygen-hydrogen balance for  $b$ :

$$b = 38$$

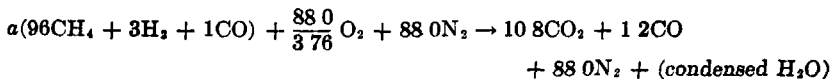
Accordingly, the mixture is



Since this is the same answer as in Example 10, it is evident that only a negligible amount of smoke must have been present

**Example 12:** (*Volumetric analysis of fuel is known*) A natural gas analyzes 96 per cent  $CH_4$ , 3 per cent  $H_2$ , and 1 per cent  $CO$ . The products of combustion by an Orsat analysis are 10.8 per cent  $CO_2$ , 1.2 per cent  $CO$ , and 88.0 per cent  $N_2$  (remainder). Set up the reaction equation

**Solution:** The partial volumes of the volumetric analyses can be considered to be moles (Arts 11-1 and 10-3)



This equation can be solved, as before, by either a carbon or an oxygen-hydrogen balance

It could also be premised that hydrogen and methane were present in the

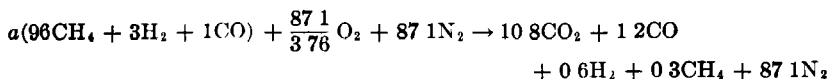
products and that, empirically,

$$\begin{aligned} \text{H}_2 &= \frac{1}{3} \text{CO} = 0.6 \text{ per cent} \\ \text{CH}_4 &= 0.3 \text{ per cent} \end{aligned}$$

With these values the apparent nitrogen is decreased to

$$\text{N}_2 = 88.0 - 0.9 = 87.1 \text{ per cent}$$

and the equation is



This latter equation should be more exact than the first solution

**11-5. Heat of Reaction.** Whenever a chemical reaction occurs, energy can be either liberated or absorbed, and this energy may be measured as a transfer of heat. For a chemical reaction at constant volume, the transfer of heat must be caused by changes in the internal energy of mixture and products if work effects are absent. The First Law energy equation requires that

$$Q - W = \Delta U \quad (\text{and } W = 0)$$

Then for reactions that begin and end at the same temperature,

$$Q_{vT} = \Delta U = U_{\text{products}} - U_{\text{mixture}} \quad (11-1)$$

Although initial and final temperatures are equal, the internal energy of the mixture does not equal the internal energy of the products because chemical internal energy is included in the evaluation.

Similarly, for a chemical reaction at constant pressure, the transfer of heat is governed by changes in internal energy and also by the work that must be done in expanding or contracting the system. Here the First Law shows, with end states at a temperature  $T$ ,

$$\begin{aligned} Q - W &= \Delta U \\ Q_p &= \Delta U + p(V_2 - V_1)]_{T,p} \\ Q_{pT} &= \Delta H = H_{\text{products}} - H_{\text{mixture}} \end{aligned} \quad (11-2)$$

Equations (11-1) and (11-2) define the *heat of reaction*: The *heat of reaction* at constant pressure and specified temperature is equal to the change in enthalpy of the system; the *heat of reaction* at constant volume and specified temperature is equal to the change in internal energy of the system.

It should be carefully noted that the heat of reaction is equal to the transfer of heat only for the prescribed conditions of Eqs. (11-1) and (11-2). In other processes between the same initial and final states,

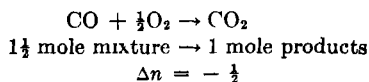
work may be transferred, such as electrical work, and the transfer of heat will be correspondingly affected, although the change in  $\Delta H$  or  $\Delta U$  will not be affected. Thus, a more appropriate name than the *heat of reaction* would be the  $\Delta H$  or  $\Delta U$  of *reaction*. Note, too, that Eqs (11-1) and (11-2) must be used with great care because the internal energy and enthalpy designated by the symbols  $U$  and  $H$  include chemical forms of internal energy. If the internal energy values in Table X (Appendix) were to be substituted in Eq. (11-1) for a temperature of 520 R, apparently the heat of reaction would be zero. This is because the values in Table X are not absolute values but, rather, are the changes in internal energy with *temperature* for a substance when no chemical or phase change occurs. Such changes in internal energy are called changes in *sensible internal energy*. The interconnecting link between the relative temperature values in Table X and the values that would include chemical internal energy is furnished by Eq. (11-1) or (11-2).

The heat of reaction at constant pressure is not necessarily equal to the heat of reaction at constant volume. The difference in these quantities is evident by subtracting Eq. (11-1) from Eq. (11-2), and, for perfect gases,

$$Q_p - Q_v \Big|_T = \Delta H - \Delta U \Big|_T = \Delta pV \Big|_T = \Delta npv \Big|_T = \Delta nR_0T \quad (11-3)$$

**Example 13:** The heat of reaction of carbon monoxide at constant pressure and a temperature of 77 F is  $-121,664$  Btu mole $^{-1}$ . Determine the heat of reaction at constant volume.

**Solution:**



From Eq. (11-3),

$$\begin{aligned} Q_p - Q_v \Big|_T &= \Delta nR_0T \\ -121,664 - Q_v &= -\frac{1}{2}(1.986)(537) \\ Q_v &= -121,131 \text{ Btu/mole (at 77 F)} \quad \text{Ans} \end{aligned}$$

**11-6. Heat of Combustion.** The heat of reaction is called the *heat of combustion* when oxygen is used to burn the fuel completely to products. The heat of combustion at constant volume can be measured by the bomb calorimeter (Fig. 11-2). The procedure of test is to place a known mass of fuel oil or crushed coal in the fuel pan and in close proximity to an ignition wire. Then, the bomb is charged with, relatively, a great amount of oxygen to a pressure of 20 or 30 atm to ensure essentially complete oxidation of the fuel into products. The



bomb is placed in the water bath while the ignition wire is connected to a battery. When the ignition wire is fused by an electric current, the fuel will react with the oxygen (burn), and the release of chemical energy will cause the temperature of the bomb and the water to increase. Heat losses from the jacket to the atmosphere are mini-

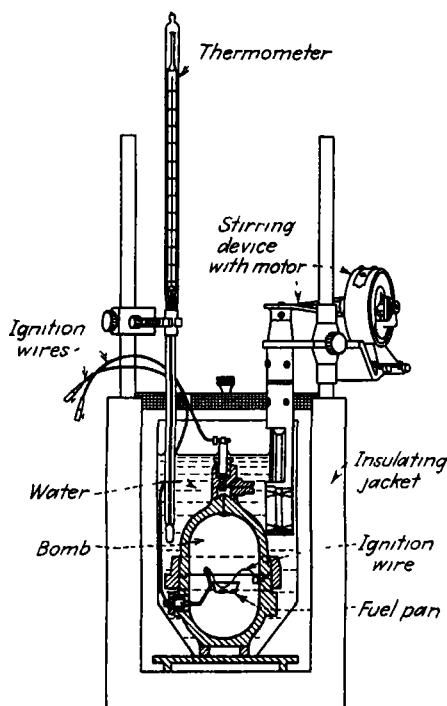


FIG 11-2 Emerson bomb calorimeter

mized by using an insulated container. Actually, with this apparatus the process is not isothermal, for this would require zero temperature rise of the water, and the amount of heat received by the water jacket is less than the heating value of the fuel by the amount of energy left in the gases in the bomb. Since the temperature rise is small, the amount of energy not transferred to the coolant is negligibly small, and the initial and final temperatures can be considered to be essentially equal.

**Example 14:** One-tenth gram of fuel is placed in a bomb calorimeter. The mass of water surrounding the bomb is 1,900 g, while the mass of the bomb and parts of the stirrer, thermometer, etc., that are also heated are equivalent to 462 g of water. If the temperature rise of the process is 0.83 F, what is the heat of combustion of the fuel? (Initial temperature of the water is 77 F)

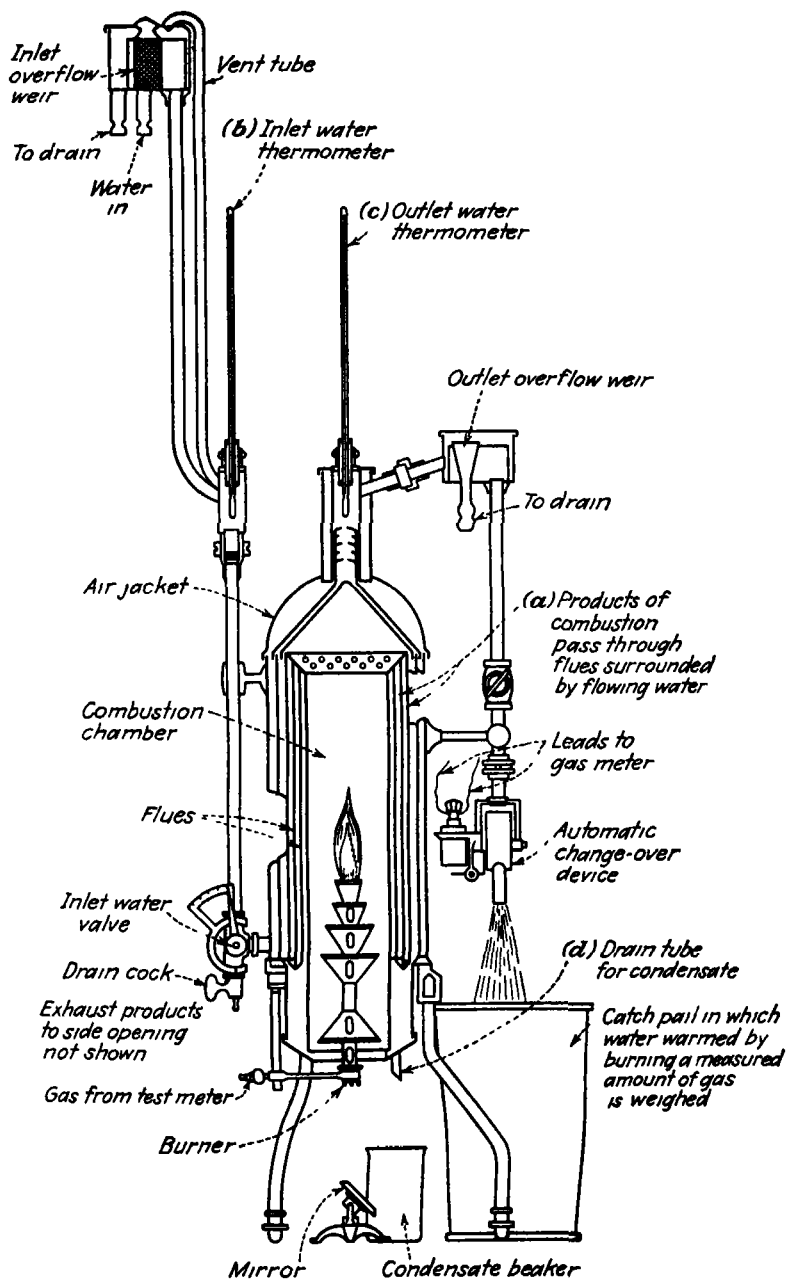


FIG 11-3 Steady-flow gas calorimeter (Precision Scientific Co)

**Solution :**

$$Q_{\text{measured}} = \frac{(\text{mass of water, bomb, etc.})(\text{heat capacity})(\text{temp. rise})}{\text{mass of fuel}}$$

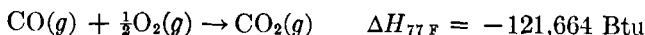
$$= \frac{(2,362 \text{ g})(10 \text{ Btu/lb}_m \text{ F})(0.83 \text{ F})}{(0.1 \text{ g})} = 19,650 \text{ Btu/lb}_m \text{ fuel}$$

Since this transfer of heat is *from* the system of fuel and oxygen, then,

$$Q_{r,77 \text{ F}} = \Delta U_{77 \text{ F}} = -19,650 \text{ Btu/lb}_m \text{ fuel} \quad \text{Ans}$$

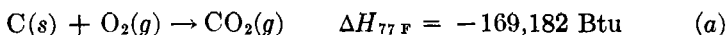
The flow system illustrated in Fig. 11-3 is generally used to find the heat of combustion at constant pressure of gaseous fuels. Here gas and air at room temperature enter the calorimeter, the volume of gas to be burned being measured by a gas meter. The products of combustion are cooled to the initial temperature by the water jacket *a*. The amount of cooling water passing through the calorimeter in a known period of time is weighed, and the temperature rise of the water is given by the temperature difference indicated by the inlet and outlet thermometers *b* and *c*. Water formed by combustion is collected at *d*. Thus, the change in enthalpy between mixture and products is measured by the quantity of heat transferred to the coolant.

**11-7. The Reaction Equation and the Standard State.** The combustion of carbon monoxide at constant pressure is shown by the equation



This equation implies the complete conversion of 1 mole of CO and  $\frac{1}{2}$  mole of O<sub>2</sub> to form 1 mole of CO<sub>2</sub> at a temperature of 77 F and at a constant pressure of 1 atm. The change in enthalpy for the process is -121,664 Btu for each mole of CO<sub>2</sub> that is formed, and this energy may be evolved as heat if no work is transferred. The phase of each substance is shown by the letter *g* which indicates the gaseous phase [and (*l*) and (*s*) are used to show the liquid and solid phases]. In the absence of information as to the state of the substances shown in the equation, it is presupposed that each substance is in its *standard state*. *The standard state is usually the stable form of the substance at the indicated temperature and at a pressure of 1 atmosphere.* The number of standard states is arbitrarily curtailed by selecting 25 C (77 F) as the standard temperature (although 18 C has also been used). Although the standard state implies unit pressure, this requirement is not essential when the gases can be considered to be ideal, for internal energy and enthalpy of the perfect gas are properties that depend only upon temperature (and the internal energy and enthalpy of real solids and real liquids are little affected by pressure).

The properties of enthalpy and internal energy are fixed by the state of the system, and therefore the change in these properties in passing from reactants to products is entirely independent of the intermediate products that may be formed or the transfers of heat and work that may accompany the change. When the heat of combustion of solid carbon at constant pressure is found by experiment to be



and also for carbon monoxide,



Then, Eq. (b) can be subtracted from Eq. (a) to yield



This procedure was possible because the  $\text{CO}_2$ , for example, was in the same state in either equation, and therefore its enthalpy in each equation had the same value. In this manner the heat of reaction can be predicted for reactions that do not yield completely oxidized products if sufficient experimental data are available for related compounds.

**11-8. Heat of Formation.** To facilitate the calculations of heats of reaction, a table of relative enthalpies can be constructed. The enthalpy of each element in the standard state is arbitrarily set equal to zero. Then, when a compound is formed from the elements, the enthalpy of the compound is equal to the  $\Delta H$  for the reaction. Thus,

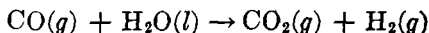


and, arbitrarily, at a datum of  $t = 77^\circ \text{F}$ ,  $p = 1 \text{ atm}$ ,

$$\begin{aligned} h_{\text{C}(s)} &= 0 \\ h_{\text{O}_2(g)} &= 0 \\ h_{\text{CO}_2(g)} &= -169,182 \text{ Btu/mole} \end{aligned}$$

The enthalpy of a compound relative to its elements is called its *heat of formation*. The standard or reference state must always be specified.

The heat of reaction can be calculated when the heat of formation is known for each compound taking part in the reaction. Consider that



and for this reaction

$$\Delta H = h_{\text{CO}_2} + h_{\text{H}_2} - h_{\text{CO}} - h_{\text{H}_2\text{O}(l)}$$

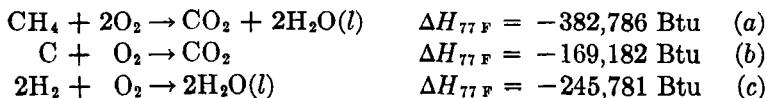
Since a table of heats of formation is merely a table of relative enthal-

pies, values can be substituted in the above equation from Table XIII (Appendix). When this is done,

$$\begin{aligned}\Delta H_{77^\circ \text{F}} &= -169,182 + 0 + 47,518 + 122,893 \\ \Delta H_{77^\circ \text{F}} &= 1,229 \text{ Btu}\end{aligned}$$

Again it is emphasized that this heat of reaction is for the standard state of Table XIII

The heat of formation of a compound can be calculated by combining the reaction equations. Thus, the relative enthalpy of methane to its elements, carbon and hydrogen, can be found from the combustion equations (Table XII, Appendix)



Upon subtracting Eq (a) from Eqs (b) and (c) it will be found that



and

$$\begin{aligned}\Delta H_{77^\circ \text{F}} &= -245,781 - 169,182 + 382,786 \\ \Delta H_{77^\circ \text{F}} &= -32,177 \text{ Btu}\end{aligned}$$

And therefore, by convention

$$\begin{aligned}h_{\text{C}(s)} &= 0 \\ h_{\text{H}_2(g)} &= 0 \\ h_{\text{CH}_4(g)} &= -32,177 \text{ Btu/mole}\end{aligned}$$

which is the heat of formation of methane

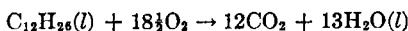
**11-9. Higher and Lower Heating Values.** Whenever a fuel contains hydrogen, one of the products of combustion will be water, which will exist either as a liquid, gas, or a two-phase mixture. If the water formed by combustion of the hydrogen in the fuel can be condensed, a greater amount of heat can be obtained from the calorimeter test than if the water existed in the vapor state. Because of this fact, two heating values can be recognized: the *higher heating value (gross)* is obtained when water formed by combustion is entirely condensed in the calorimeter test; the *lower heating value (net)* of the fuel is obtained when water formed by combustion exists entirely in the vapor state. The difference between these two heating values is equal to the latent energy of vaporization of the water at the test temperature.

In the constant-volume calorimeter, a few drops of water can be placed in the bomb to saturate the oxygen atmosphere before the test

is begun. In this manner, a higher heating value of the fuel is obtained because (practically) all the water formed by combustion must condense and the latent internal energy of vaporization of the water is transferred to the coolant.

**Example 15:** Calculate the lower heating value for the fuel oil in Example 14 if the formula for the fuel is  $C_{12}H_{26}$ . Assume that the atmosphere of the bomb was initially saturated with water and therefore the answer in Example 14 was a higher heating value that can be considered to be for standard states of the mixture and products.

**Solution:**



and

$$\frac{13(18)}{170} = 1.375 \text{ lb}_m \text{ water formed per lb}_m \text{ fuel burned}$$

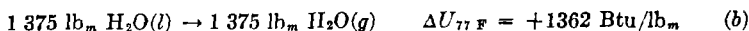
In contracted form,



From the Steam Tables, at 77 F

$$\begin{aligned} h_{fg} &= 1050.4 \text{ Btu/lb}_m \\ u_{fg} &= h_{fg} - pv_{fg} = 1050.4 - \frac{0.4593(144)(694.9)}{778.2} \\ &= 991.4 \text{ Btu/lb}_m \text{ water} \end{aligned}$$

and for 1.375 lb<sub>m</sub> H<sub>2</sub>O



Equations (b) and (a) could be added together if each component were in the same state. This requirement is not fulfilled because the data of Eq. (b) are for a pressure of 0.4593 psia, and in the test represented by Eq. (a) it is quite probable that the partial pressure of the water vapor was not 0.4593 psia. This discrepancy (and the failure of the test and the calculated value to be for the standard state) is not serious because the internal energy is influenced more by temperature than by pressure. Hence, Eqs. (a) and (b) are added, and, within the allowable error of the experiment,



(for liquid fuel and vaporized water products)

In the constant-pressure calorimeter, no water vapor can condense if the gases leaving the calorimeter are at a sufficiently high temperature. The constant-pressure calorimeter will give directly the lower heating value if the exit temperature is above the condensation (dew point) temperature of the combustion products and the incoming air and fuel are warmed to that temperature. However, most calorimeters are operated to give the higher heating value by cooling the

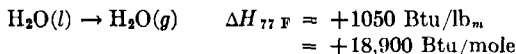
products down to the initial conditions. Correcting for any additional (or less) moisture remaining in the products over that supplied in the fuel and air, by adding (or subtracting) the latent heat of vaporization not delivered to the calorimeter from these sources, gives the higher heating value at the given test temperature

**Example 16:** The heat of combustion of  $C_8H_{18}(g)$  at constant pressure is  $-2,199,548$  Btu mole $^{-1}$  at 77 F. This value is for gaseous products the lower heating value. Determine the higher heating value for gaseous and for liquid fuels

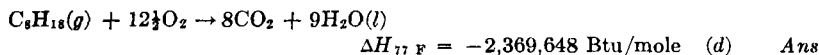
**Solution:**



From the Steam Tables,  $h_{f,0}$  at 77 F is

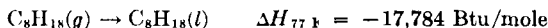


When this equation is multiplied by 9 and subtracted from Eq (c),



This is the higher heating value at constant pressure for gaseous fuel

To convert this equation to liquid fuel, Table XII (Appendix) shows



Subtracting this equation from Eq (d)



This, too, is a higher heating value but for liquid fuel

(The comments in Example 15 as to the approximations made in combining the equations apply as well to this example)

The heat of combustion of a fuel at constant pressure is, in many instances, a measure of the heat that is transferred to a thermodynamic cycle. For this reason the calculated thermal efficiency of the cycle will depend on the value that is assigned to the heat of combustion. The higher heating value represents the true amount of heat that can be transferred from the reaction, and therefore it is the value that should be used in calculating efficiencies. However, the heat that theoretically can be attained by condensing the water formed by combustion is, practically, not attainable. For this reason thermal-efficiency calculations are sometimes based upon the lower heating value of the fuel. In comparing the thermal efficiencies of different cycles it is well to ensure that the same basis of comparison has been made, for, otherwise, misleading conclusions may be drawn.

**11-10. Heat of Reaction and Temperature.** After the heat of reaction has been determined at one temperature, it can be readily calculated for any other temperature. Consider Eq (11-1).

$$Q_{vT_1} = (U_{\text{products}} - U_{\text{mixture}})_{T_1}$$

The same form of equation can be written for the heat of reaction at  $T_2$

$$Q_{vT_2} = (U_{\text{products}} - U_{\text{mixture}})_{T_2}$$

and when one equation is subtracted from the other,

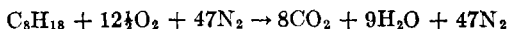
$$Q_{vT_2} - Q_{vT_1} = \Delta U_{\text{products}} \Big|_{T_1}^{T_2} - \Delta U_{\text{mixture}} \Big|_{T_1}^{T_2} \quad (11-4a)$$

Equation (11-2) can be treated in the same manner

$$Q_{pT_2} - Q_{pT_1} = \Delta H_{\text{products}} \Big|_{T_1}^{T_2} - \Delta H_{\text{mixture}} \Big|_{T_1}^{T_2} \quad (11-4b)$$

**Example 17:** The heat of combustion of octane at constant volume is  $-2,203,279$  Btu mole $^{-1}$  at 537 R for gaseous fuel and gaseous products. What will be the heat of reaction at 1000 R? (Assume that all gases behave as perfect gases.)

**Solution:** The combining equation is



Since nitrogen appears in both reactants and products, it need not be considered. Equation (11-4a) can be evaluated from the heat-capacity relationships of Table IIB since the terms on the right-hand side of the equation do not involve chemical changes

$$\begin{aligned} \Delta U_{\text{products}} &= 8 \text{ moles CO}_2 \int_{537}^{1000} c_v dT + 9 \text{ moles H}_2\text{O} \int_{537}^{1000} c_v dT \\ \Delta U_{\text{mixture}} &= 1 \text{ mole C}_8\text{H}_{18} \int_{537}^{1000} c_v dT + 12\frac{1}{2} \text{ moles O}_2 \int_{537}^{1000} c_v dT \end{aligned}$$

Upon integrating these relationships and substituting in Eq (11-4a), the heat of reaction at 1000 R can be determined

An alternate and easier method is to use the internal energy tables, Appendix Table X (which were constructed from the heat-capacity relationships in Table IIB)

$$\begin{aligned} \Delta U_{\text{products}} &= 8(U_{1000} - U_{537})_{\text{CO}_2} + 9(U_{1000} - U_{537})_{\text{H}_2\text{O}} \\ &= 8(3852 - 118) + 9(3009 - 104) = 56,017 \text{ Btu} \\ \Delta U_{\text{mixture}} &= 1(U_{1000} - U_{537})_{\text{C}_8\text{H}_{18}} + 12\frac{1}{2}(U_{1000} - U_{537})_{\text{O}_2} \\ &= (24,773 - 640) + 12\frac{1}{2}(2539 - 85) = 54,808 \text{ Btu} \end{aligned}$$

Substituting these values in Eq (11-4a),

$$\begin{aligned} Q_{v1000} - Q_{v537} &= \Delta U_{\text{products}} \Big|_{537}^{1000} - \Delta U_{\text{products}} \Big|_{537}^{1000} \\ Q_{v1000} &= -2,203,279 + 56,017 - 54,808 \\ Q_{v1000} &= -2,202,070 \text{ Btu/mole (for gaseous fuel and products)} \quad \text{Ans} \end{aligned}$$



**11-11. Theoretical Flame Temperatures.** In computing theoretical flame temperatures, general relationships can be derived from the principle of conservation of energy, the First Law. Consider a constant volume and adiabatic combustion of a fuel-air mixture.

$$Q - W = \Delta U$$

Then,

$$Q = 0 \quad W = 0 \quad \Delta U = 0$$

and therefore

$$U_{\text{products } T_2} = U_{\text{mixture } T_1} \quad (a)$$

The heat of reaction is defined

$$Q_{vT_1} = U_{\text{products } T_1} - U_{\text{mixture } T_1} \quad (11-1)$$

and substituting Eq (a) in Eq (11-1),

$$Q_{vT_1} = -\Delta U_{\text{products}} \Big]_{T_1}^{T_2} \quad (11-5a)$$

while, at constant pressure,

$$Q_{pT_1} = -\Delta H_{\text{products}} \Big]_{T_1}^{T_2} \quad (11-5b)$$

In words, Eq (11-5) implies that the combustion process can be assumed equivalent to burning the mixture completely into products at the initial temperature  $T_1$ , and, with the heat of reaction so obtained, the products can be raised to the final temperature  $T_2$ . This procedure is possible because, it should be recalled, internal energy (or enthalpy) is a property that is determined by the state. Thus, irrespective of the actual series of states in the real combustion process, a hypothetical series of states can be assumed between the two end states.

Equation (11-5) can be converted into a different form by substituting Eq (11-4) into Eq (11-5)

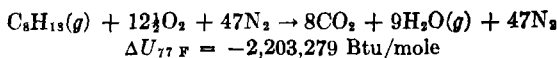
$$Q_{vT_1} = -\Delta U_{\text{mixture}} \Big]_{T_1}^{T_2} \quad (11-6a)$$

$$Q_{pT_1} = -\Delta H_{\text{mixture}} \Big]_{T_1}^{T_2} \quad (11-6b)$$

Equation (11-6) implies that the mixture is raised in temperature from  $T_1$  to  $T_2$  and then completely converted into products. The heat of reaction available to perform this task is that evaluated at the temperature level  $T_2$ . Since this value cannot be computed until the unknown temperature  $T_2$  has been found, Eq. (11-6) is not as readily used as Eq (11-5)

**Example 18:** Compute the combustion temperature for complete combustion of vaporized octane with the theoretical amount of air at constant volume from an initial temperature of 537 R

**Solution:** The combining equation is



The lower heating value is selected because then the products are all gases and from Table X (Appendix)

$$u_{\text{products}} = 8\text{CO}_2 + 9\text{H}_2\text{O}(\text{g}) + 47\text{N}_2$$

$$U_{\text{products, } T_1} = 8(118) + 9(104) + 47(82.5) = 5,757 \text{ Btu}$$

and by Eq. (11-5a)

$$U_{\text{products, } T_2} = U_{\text{products, } T_1} - Q_{v, T_1}$$

$$= 5757 + 2,203,279 = 2,209,036 \text{ Btu}$$

Assume  $T_2 = 5300 \text{ R}$

$$U_{\text{products, } T_2} = 8(55,265) + 9(43,187) + 47(29,648)$$

$$= 2,224,259 \text{ Btu}$$

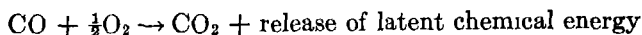
Assume  $T_2 = 5200 \text{ R}$

$$U_{\text{products, } T_2} = 2,171,627 \text{ Btu}$$

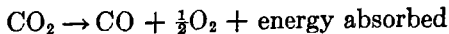
Upon interpolating,

$$T_2 = 5271 \text{ R} \quad \text{Ans.}$$

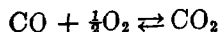
**11-12. Chemical Equilibrium.** The theoretical temperature of complete combustion, which was computed in Art. 11-11, cannot be attained because reaction is never complete. For example, the reaction of carbon monoxide and oxygen yields carbon dioxide with liberation of energy that raises the temperature



But  $\text{CO}_2$  will *dissociate*, especially at high temperatures, with absorption of energy:



Thus, in the reaction of carbon monoxide and oxygen,  $\text{CO}_2$  is formed and the temperature is increased. But, since  $\text{CO}_2$  dissociates into  $\text{CO}$  and  $\text{O}_2$ , a limiting temperature is attained when the reaction has the same rate for either direction; the reaction is then in *chemical equilibrium*:

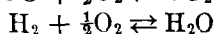
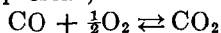


That is, definite proportions of  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  are present in the equilibrium mixture at each temperature; at low temperatures the proportion of  $\text{CO}_2$  is high, while at high temperatures the proportion of  $\text{CO}_2$  is low. For this reason, the theoretical temperature calculated

upon the assumption that the mixture is completely converted into products cannot be attained because the temperature rise of combustion limits the degree of completion of the reaction and therefore limits the release of chemical energy

In the calorimeters described previously, chemical equilibrium may have prevented the containers from reaching maximum temperatures, but this was immaterial because the important factor was to ensure that the primary reaction went essentially to completion. This degree of completion was secured by operating the calorimeters at room temperature where dissociation of combustion products is negligible (and by supplying an overabundance of oxygen)

The products of combustion that may dissociate are usually  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (although at very high temperatures molecular dissociation to the atoms will also be present)



Let  $x$  and  $y$  be the amount of dissociation of 1 mole of  $\text{CO}_2$  and 1 mole of  $\text{H}_2\text{O}$ , the reaction from mixture to equilibrium products will be

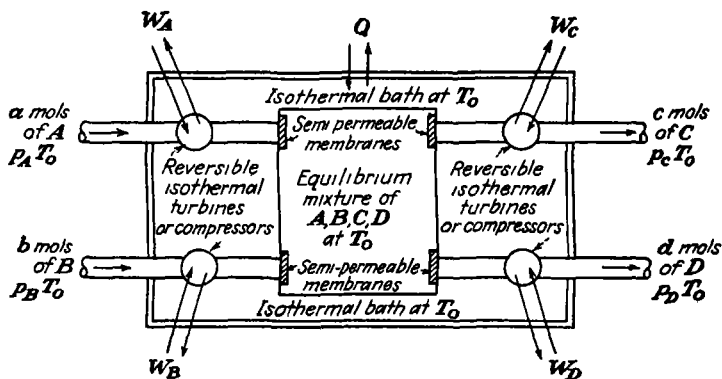
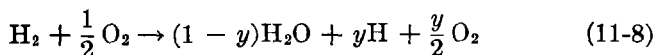
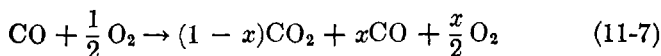
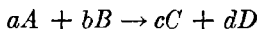


FIG 11-4. A van't Hoff equilibrium box

**11-13. The Equilibrium Constant.** The reaction at chemical equilibrium is characterized by the presence of both mixture and products, and here the problem is to find an *equilibrium constant* that will define the degree of completion of the reaction. The form of this constant can be determined by studying a reversible and isothermal reaction

In Fig 11-4 is illustrated a van't Hoff reaction box that contains ideal gases  $A$ ,  $B$ ,  $C$ , and  $D$  in chemical equilibrium. The equilibrium box has four semipermeable membranes that possess the unique property of being permeable only to one substance. Now, as reactants  $A$  and  $B$  flow into the system, they are isothermally expanded or compressed to the partial pressures of  $A$  and  $B$  in the equilibrium mixture ( $p'_A$ ,  $p'_B$ ). The addition of these reactants will cause products  $C$  and  $D$  to be formed (a catalyst can be premised to be present to speed the reaction), and these products are removed through their respective semipermeable membranes. The products are then isothermally compressed or expanded to the final pressure. (Although, upon removal, the pure products will have a tendency to dissociate into the original mixture, it will be assumed that this reaction is very slow if only because of the absence of a catalyst.)

The reaction equation for  $a$  moles of  $A$ ,  $b$  moles of  $B$  to form  $c$  moles of  $C$  and  $d$  moles of  $D$  is



The isothermal work of each turbine in Fig 11-4 can be evaluated

$$W = nR_0T \ln \frac{p_1}{p_2} \quad (8-7b)$$

and therefore the work for the system containing four turbines is

$$\sum W \Big|_{T, \text{flow}} = R_0T \left( a \ln \frac{p_A}{p'_A} + b \ln \frac{p_B}{p'_B} + c \ln \frac{p'_C}{p_C} + d \ln \frac{p'_D}{p_D} \right)$$

This equation reduces to

$$\sum W \Big|_{T, \text{flow}} = R_0T \left[ \ln \frac{p'_C p'_D}{p_A^a p_B^b} - \ln \frac{p_C p_D}{p_A^a p_B^b} \right] \quad (11-9a)$$

Equation (11-9a) can be further simplified by noting that  $p_A$ ,  $p_B$ ,  $p_C$ , and  $p_D$  can be arbitrarily selected without affecting the chemical equilibrium. Selecting, then, the standard-state value of 1 atm allows the second term to disappear (since  $\ln 1 = 0$ ). Thus, the reversible isothermal work for the reaction, with all reactants initially at a standard state of 1 atm and all products finally at a standard state of 1 atm, is

$$\sum W \Big|_{T, p^\circ, \text{flow}} = R_0T \ln \frac{p'_C p'_D}{p_A^a p_B^b} = R_0T \ln K_p \quad (11-9b)$$

$$K_p = \frac{p'_C p'_D}{p_A^a p_B^b} \quad (11-10a)$$

Equation (11-10a) defines the *equilibrium constant*  $K_p$ , which shows the interrelationships between the perfect-gas components of the equilibrium mixture. It can be determined by measuring the partial pressures of the components of the equilibrium mixture. The equilibrium constant is a function of the temperature; values for certain reactions can be found in Fig. VI (Appendix).

**Example 19:** Experimental measurements show that 1 mole of  $\text{H}_2\text{O}$  is 5 per cent dissociated into hydrogen and oxygen at a pressure of 147 psi. Calculate the equilibrium constant and determine the temperature.

**Solution:** The complete reaction equation is



Since the  $\text{H}_2\text{O}$  is one-twentieth dissociated, the mixture at equilibrium is

$$0.95\text{H}_2\text{O} + 0.05\text{H}_2 + 0.025\text{O}_2 = 1.025 \text{ moles}$$

The partial pressure of the constituents, in atmospheres, is

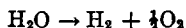
$$\begin{aligned} \text{H}_2\text{O} \left( \frac{\text{moles of H}_2\text{O}}{\text{moles mixture}} \right) \times \left( \frac{\text{total pressure in psi}}{14.7 \text{ psi/atm}} \right) &= \frac{0.95}{1.025} (10) \\ &= 9.268 \text{ atm} \\ \text{H}_2 \frac{0.05}{1.025} (10) &= 0.488 \text{ atm} \quad \text{O}_2 \frac{0.025}{1.025} (10) = 0.244 \text{ atm} \end{aligned}$$

Based upon Eq. (a), the equilibrium constant would be

$$K_p = \frac{p'_{\text{H}_2\text{O}}}{(p'_{\text{H}_2})(p'_{\text{O}_2})^{\frac{1}{2}}} = \frac{9.268}{0.488(0.244)^{\frac{1}{2}}} = 38.4 \quad \text{Ans}$$

Figure VI (Appendix) shows that this value corresponds to a temperature of 5140 R. *Ans*

If Eq. (a) had been written in the form



the equilibrium constant would then be the reciprocal of 38.4 or 0.026. If Eq. (a) had been expressed as



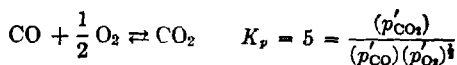
the equilibrium constant for Eq. (b) would then be

$$K_p = \frac{(p'_{\text{H}_2\text{O}})^2}{(p'_{\text{H}_2})^2(p'_{\text{O}_2})} = \frac{(9.268)^2}{(0.488)^2(0.244)} = 1,480$$

These examples emphasize that the equilibrium constants are evaluated for a definite form of the reaction equation, and this form must be known before the constant can be used in computations. Also, the units for the partial pressures must be known. Figure VI (Appendix) shows not only the equilibrium constants but also the equations and units upon which the constants are based.

**Example 20:** Calculate the degree of dissociation of 1 mole of  $\text{CO}_2$  at 5170 R for total pressures of 1 and 10 atm.

**Solution** • Figure VI (Appendix) shows, at 5170 R,



The equilibrium mixture is [Eq (11-7)]

$$(1 - x)\text{CO}_2 + x\text{CO} + \frac{x}{2} \text{O}_2 = 1 + \frac{x}{2} \text{ moles} = n$$

The partial pressures of the constituents are

$$\begin{aligned} p'_{\text{CO}_2} &= \frac{\text{moles CO}_2}{\text{moles mixture}} \times \text{total pressure in atmospheres} \\ &= \left( \frac{1 - x}{n} \right) p \\ p'_{\text{CO}} &= \left( \frac{x}{n} \right) p \\ p'_{\text{O}_2} &= \left( \frac{x}{2n} \right) p \end{aligned}$$

And, for  $p = 1$  atm,

$$K_p = \frac{\left( \frac{1 - x}{n} \right) p}{\left( \frac{x}{n} \right) p \left( \frac{x}{2n} \right)^{\frac{1}{2}} p^{\frac{1}{2}}} = \frac{(1 - x)(2 + x)^{\frac{1}{2}}}{x^{\frac{3}{2}}} = 5.00$$

After squaring each side and reducing,

$$\begin{aligned} 24x^3 + 3x &= 2 \\ x &= 0.344 \text{ or } 34.4 \text{ per cent dissociation of the CO}_2 \quad \text{Ans} \end{aligned}$$

At a pressure of 10 atm,

$$K_p = \frac{(1 - x)(2 + x)^{\frac{1}{2}}}{x^{\frac{3}{2}}(10)^{\frac{1}{2}}} = 5.00$$

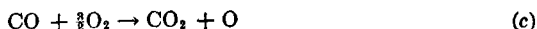
Upon solution

$$x = 0.18, \text{ or } 18 \text{ per cent dissociation of the CO}_2 \quad \text{Ans}$$

Note that an increase in pressure tends to shift the equilibrium to a smaller volume. Since in this reaction the volume of products is less than the volume of the mixture, the degree of completion is increased by an increased pressure. The opposite effect is encountered if the products have a greater volume than the mixture.

**Example 21:** If three times the correct amount of oxygen is supplied in burning CO, what will be the percentage of dissociation of the  $\text{CO}_2$  at 5170 R and a total pressure of 1 atm?

**Solution:** The combining equation is



The mixture at equilibrium is

$$(1 - x)\text{CO}_2 + x\text{CO} + \frac{x}{2} \text{O}_2 + \text{O} = 2 + \frac{1}{2} x \text{ moles} = n \quad (d)$$

The partial pressure of the constituents

$$p'_{\text{CO}_2} = \frac{(1-x)}{n} (p)$$

$$p'_{\text{CO}} = \frac{x}{n} (p)$$

$$p'_{\text{O}_2} = \frac{x+2}{2n} (p)$$

For Eq (c)

$$K_p = \frac{(p'_{\text{CO}_2})(p'_{\text{O}_2})}{(p'_{\text{CO}})(p'_{\text{O}_2})^{\frac{1}{2}}} = \frac{p'_{\text{CO}_2}}{p'_{\text{CO}}(p'_{\text{O}_2})^{\frac{1}{2}}} = \frac{(1-x)}{x \left( \frac{2+x}{4+x} \right)^{\frac{1}{2}}} = 5.00$$

Squaring and simplifying result in

$$24x^2 + 48x^2 + 7x = 4$$

Solving by trial and error,

$$x = 0.22, \text{ or } 22 \text{ per cent dissociation} \quad \text{Ans}$$

Compare with Example 20. The presence of excess oxygen drives the reaction farther toward completion. Too, the excess oxygen would lower the flame temperature and so decrease the tendency toward dissociation.

**11-13. The Equilibrium Constant (Continued).** Suppose that the solid or liquid phase of one of the reactants is also present in the equilibrium mixture. In this instance the partial pressure is uniquely determined by the vapor pressure which is independent of the amount of material present (Art 10-7). The form of the equilibrium constant can be found by the system of Fig 11-4. Consider that ideal gases *A*, *B*, *C*, and *D* are in equilibrium in the reaction box and a small amount of substance *A* in the liquid (or solid) phase is also present. The pressure of ideal gas *A* in the equilibrium mixture is the vapor pressure of the substance. Let reactant *A* enter the system in the liquid (or solid) phase and undergo an isothermal expansion to its partial pressure in the reaction box. The work obtained from this process will be extremely small [of amount, closely  $-v\Delta p$  see Eq (4-2) or Example 22d] because the specific volume of the liquid (or solid) is small and remains essentially constant during the process. The liquid (or solid) can be vaporized (or sublimed) at constant pressure by transfer of heat from the surroundings and the vapor (gas) introduced into the equilibrium box through a semipermeable membrane. The work obtained from this system is [see derivation of Eq (11-9a)]

$$\sum W \Big|_{T, \text{flow}} = R_o T \left( \ln \frac{p'_c p'_d}{p'_b} - \ln \frac{p^c p^d}{p^b} \right) \quad (11-9c)$$

Since the insignificant amount of work obtained by expanding the liquid to its vapor pressure can be ignored, the partial pressure of the liquid (or solid) phase (*A*) does not appear in this equation. Note, too, that the partial pressure of *A* in the equilibrium mixture is a constant and therefore independent of the total pressure in the reaction box. Equation (11-9c) can be simplified by selecting the standard-state pressure of 1 atm for the initial and final states

$$\sum W \Big]_{T, p^\circ_{\text{flow}}} = R_0 T \ln \frac{p'_c p'_d}{p'_b} = R_0 T \ln K_p \quad (11-9d)$$

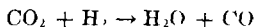
$$K_p = \frac{p'_c p'_d}{p'_b} \quad (11-10b)$$

Equation (11-10b) defines the equilibrium constant for cases where one (or more) of the reactants is in the solid or liquid state at equilibrium, the partial pressure of that component does not appear in the equation

**11-13 The Equilibrium Constant (Continued).** The equilibrium-constant equations for the combustion of  $H_2$  and CO are

$$K_{p_{H_2O}} = \frac{p'_{H_2O}}{p'_{H_2} (p'_{O_2})^{\frac{1}{2}}} \quad K_{p_{CO_2}} = \frac{p'_{CO_2}}{p'_{CO} (p'_{O_2})^{\frac{1}{2}}}$$

Each of these equations must be satisfied if the mixture at equilibrium contains  $CO_2$ ,  $H_2O$ , and their dissociation products. However,  $H_2O$  and CO react to form  $CO_2$  and  $H_2$



This is sometimes called a *water gas reaction*, and the equilibrium constant for this reaction must also be satisfied

$$K_{p_{wg}} = \frac{p'_{CO} p'_{H_2O}}{p'_{CO_2} p'_{H_2}} = \frac{K_{p_{H_2O}}}{K_{p_{CO_2}}}$$

Note that the total number of moles does not change during this reaction and therefore the reaction is independent of pressure and the partial pressures can be replaced by the moles of substances present. But the mole ratio of CO to  $CO_2$  and  $H_2O$  to  $H_2$  in any mixture is by definition [Eqs. (11-7) and (11-8)]

$$\frac{\text{moles CO}}{\text{moles } CO_2} = \frac{x}{1-x} \quad \frac{\text{moles } H_2O}{\text{moles } H_2} = \frac{1-y}{y}$$

and therefore

$$K_{p_{wg}} = \frac{x(1-y)}{y(1-x)} \quad (11-11)$$

This reaction is frequently of importance in combustion engine work because all four substances are products of combustion from the engine. The speed of this reaction or the *reaction rate* is relatively slow below 1600 F, for this reason, if the equilibrium mixture is quickly cooled, the same ratio of concentrations will be maintained at the low temperature as existed before at the high temperature. In other words, the equilibrium may not shift to the conditions requested by the low temperature unless there is a measurable rate of reaction. Thus, if carbon monoxide and oxygen are mixed together at room temperature, an insignificant amount of carbon dioxide is formed because the reaction rate is almost zero. But the tendency toward a change is strong because the equilibrium constant for room temperature predicts that a large amount of carbon dioxide is required for the equilibrium mixture. In this instance a spark or a catalyst can be used to overcome the inertness of the system and so approach the equilibrium state.



**11-14. The Heat Reservoir and the Combustion of Fuel.** The creation of a heat reservoir for the thermodynamic cycle can be accomplished by burning a fuel, such as coal or fuel oil, with atmospheric air. A flow process will be premised because of the large quantities of heat that are demanded by commercial systems. Thus, in Fig 11-5 air and fuel at atmospheric temperature and pressure enter the system and an irreversible mixing process occurs. The mixture is not in

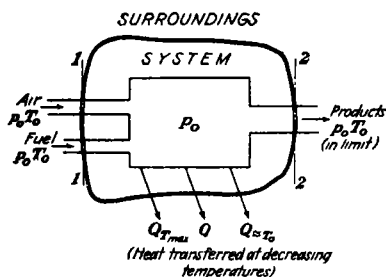


FIG 11-5 System of combustion furnace

chemical equilibrium, but the inertness of the system prevents reaction until a spark or a flame is present. An irreversible chemical reaction then takes place with the attainment of a high temperature and, perhaps finally, a state of chemical equilibrium. When heat is transferred from this finite heat reservoir, the temperature of the gases falls, succeeding transfers of heat

taking place at decreasing temperatures, until the products, in the limit, are reduced to the temperature of the surroundings—the earth or its atmosphere. For this system and irreversible process, the First Law equation shows that

$$Q = H_2 - H_1]_{T_0} \quad \text{or} \quad -Q = H_1 - H_2]_{T_0}$$

The transfer of heat will be equal to the heat of reaction of the fuel at  $T_0$  (the heating value) only if the mixture is completely converted into products<sup>1</sup>. That this conversion is theoretically approached is shown by the equilibrium constant. At 60 F the equilibrium constants for  $H_2O$  and  $CO_2$  are (Fig VI, Appendix)

$$K_{p_{H_2O}} = \frac{p'_{H_2O}}{p'_{H_2}(p'_{O_2})^{\frac{1}{2}}} = 10^{40} \quad K_{p_{CO_2}} = \frac{p'_{CO_2}}{p'_{CO}(p'_{O_2})^{\frac{1}{2}}} = 10^{48}$$

and therefore these reactions should be practically complete if chemical equilibrium is maintained throughout the furnace. Of course, this latter condition is not fulfilled in the real furnace because of the speed of the process, but the values for the equilibrium constants indicate that in an ideal furnace the reactions can be considered to be essen-

<sup>1</sup> Since the products leave as a mixture, the partial pressure of each product is less than atmospheric, and therefore the products are not in standard states. However, the change in enthalpy with pressure is insignificant, being zero for ideal gases.

tially complete when the temperature has been reduced to  $T_0$ . Thus, the heating value of the fuel measures, quite accurately, the maximum transfer of heat that can theoretically be attained by burning fuel with at least the theoretical amount of air. The usual furnace can supply about 85 per cent of this maximum to a thermodynamic cycle, while the remainder is "lost" to the surroundings; the *efficiency* of the furnace, then, is 85 per cent.

The creation of the heat reservoir is only the first step in the production of power. The heat transferred from the heat reservoir to a thermodynamic cycle cannot entirely be transformed into work because the *availability* of the heat is not determined by the calorimeter heating value, this was shown by the Second Law in Example 5 of Chapter V. For this reason the maximum work that can be realized from a thermodynamic cycle that uses, for a heat reservoir, a system that burns fuel, must be far less than the heat of reaction of the fuel.

Moreover, the highest possible temperature must be attained in the furnace if the availability of the transferred heat is to be a maximum. This ideal temperature is not reached because combustion is incomplete and excess air is present. The excess air is a necessary evil because the fuel-air mixture is never entirely homogeneous and therefore an excess of air, which is cheap, enables nearly all of the fuel, which is relatively expensive, to be burned. Too, the highest feasible combustion temperature that the walls of the furnace can successfully face (but not reach) over long periods of time is approximately 3000 F.

One other condition prevents the full availability of the heat from being realized. It is neither practical nor desirable to cool the gases to the surrounding temperature, for this would require an infinitely large heat exchanger, and water vapor would condense and so cause corrosion. This corrosion would be especially serious when sulphur dioxide appeared as a product of combustion because sulphur dioxide and water react to form sulphurous acid. For these reasons the gases leave the practical furnace at a temperature of about 300 F (although exit temperatures of 400 to 700 F are not uncommon).

It is well to note that the system of furnace, boiler, turbine, condenser, and pump is not a thermodynamic cycle even though the four latter components, by themselves, form such a cycle. The addition of the furnace to the cycle creates a new system, and this system is noncyclic because the fuel-air mixture entering the system undergoes a chemical change that is never restored.

**11-15. The Free Energy.** The amount of work that can be obtained from a system is restricted, of course, by the process. How-

ever, for any nonflow process (changes in kinetic or potential energy are assumed, for simplicity, to be absent) the First Law equation shows that

$$\begin{aligned} Q - W &= \Delta U \\ -W_{\text{rev or irrev}} &= \Delta U - Q \end{aligned}$$

The maximum work is obtained from the system (or the minimum work is delivered to the system) when the process is reversible, and, for this restriction,

$$Q_{\text{rev}} = \int T dS$$

and therefore

$$-W_{\text{rev}} = \Delta U - \int T dS \quad (a)$$

Equation (a) can be transformed into a number of forms that show the maximum (or the minimum) work transfers for *special processes*. For example, suppose that the reversible process begins and ends at a temperature  $T$  and that all heat transfers occur at this temperature, here Eq (a) reduces to

$$-W_{\text{rev nonflow}} \Big]_T = \Delta U - T\Delta S \quad (b)$$

If it is specified that the initial and final pressures are equal, then that part of the work that is used to expand or contract the system is equal to

$$p(V_2 - V_1) = p_2V_2 - p_1V_1$$

When this amount is subtracted from Eq (b), the net or useful work is obtained (work other than that of expansion or contraction)

$$-W_{\text{rev net nonflow}} \Big]_{T, p} = \Delta U + \Delta pV - T\Delta S = \Delta H - T\Delta S \quad (c)$$

In similar manner, the work of the reversible-flow process can be evaluated (Again, for simplicity, kinetic- and potential-energy changes will be neglected) Here the First Law equation is

$$Q - W_{\text{rev or irrev}} = \Delta H$$

and for reversible transfers of heat at a constant boundary temperature  $T$

$$-W_{\text{rev flow}} \Big]_T = \Delta H - T\Delta S \quad (d)$$

This is the work that can be obtained from an isothermal flow process wherein changes in kinetic and potential energies are negligible.

There are two "work" functions that are defined as

$$G = H - TS \quad (11-12a)$$

$$A = U - TS \quad (11-13a)$$

The function  $G$  is called the *free energy* or the *Gibb's free energy*; it is designated by the symbol  $G$  (and also by  $F$  and  $Z$ ). The function  $A$  is called the *maximum work* (but not in this chapter) or the *Helmholtz free energy*; it is designated by the symbol  $A$  (and sometimes by  $\psi$ ). Note that the change in these properties for a system at constant initial and final temperature is given by

$$\Delta G]_T = \Delta H - T\Delta S \quad (11-12b)$$

$$\Delta A]_T = \Delta U - T\Delta S \quad (11-13b)$$

Equations (11-12b) and (11-13b) allow Eqs (b), (c), and (d) to be expressed as

$$W_{\text{rev nonflow}}]_T = -\Delta A \quad (11-14)$$

$$W_{\text{rev net nonflow}}]_{T,p} = -\Delta G \quad (11-15)$$

$$W_{\text{rev flow}}]_T = -\Delta G \quad (11-16)$$

The importance of Eqs (11-14), (11-15), and (11-16) lies in the fact that most engineering processes start and end at essentially the same temperature and pressure. In Fig 11-6 is illustrated a flow diagram that can be interpreted to be any one of the three main power-producing systems. Here air and fuel enter the system while work and heat are transferred to the surroundings, the atmosphere. The products leave at the pressure and temperature of the atmosphere. If these processes were reversibly operated, Eq (11-16) shows that the work would be equal to  $-\Delta G$ .

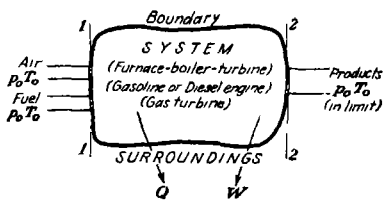


FIG 11-6 General heat power system

$$W_{\text{rev flow}}]_T = G_1 - G_2 = -\Delta H + T\Delta S \quad (11-16)$$

But Eq (11-16) also indicates that the work obtained from the process is greater or less than the negative of the heat of reaction ( $-\Delta H$ ) according as the sign of  $\Delta S$  is positive or negative. For the

reversible process, an increase in entropy shows that heat has been transferred to the system from the surroundings (the atmosphere), and by this aid the work output has been increased to a value *greater* than the negative of the heat of reaction. It should be remembered that the discussion in Art 11-14 showed that the work, obtained by burning fuel in a furnace (an irreversible process) and then transferring heat to a cycle, will be much less than the heat of reaction. But in this article a reversible process (but not a cycle) has been defined that will produce far more work than that obtained indirectly from the irreversible combustion process. However, a practical means of obtaining this ideal work is not so easily found. For example, the isothermal and reversible process of Fig 11-4 would also yield work of amount  $-\Delta G$ . But the process must be run at an infinitely slow speed if the isothermal transfer of heat between system and atmosphere is to be reversible (and semipermeable membranes must also be discovered). Although Eqs (11-14), (11-15), and (11-16) predict a far greater work output than it is possible to obtain from industrial processes, still, the development of a process that can approach reversible operation is not easily accomplished.

The change in free energy with a change in pressure is readily computed. Since  $G$  is a property, then for unit mass ( $g$ ) of any one substance (and the symbol  $g$  also denotes a chemical change)

$$g = h - Ts$$

$$dg = dh - Tds - sdT$$

Substituting

$$dh = Tds + vdp \quad (5-14b)$$

yields, for constant temperature,

$$dg]_T = vdp \quad (11-17)$$

For perfect gases, Eq (11-17) integrates to

$$\Delta g]_T = -R_0T \ln \frac{p_1}{p_2} \quad (11-18)$$

a result that could have been surmised from Art 11-13.

The *standard free energy change* is defined as the change in the property  $G$  between the products in their standard states and the reactants in their standard states. As before, the standard state is the phase that is normal at 1 atm pressure and at the specified temperature. For this reason Eq (11-9b), which defines the equilibrium constant, is also equal to (but of opposite sign from) the standard free

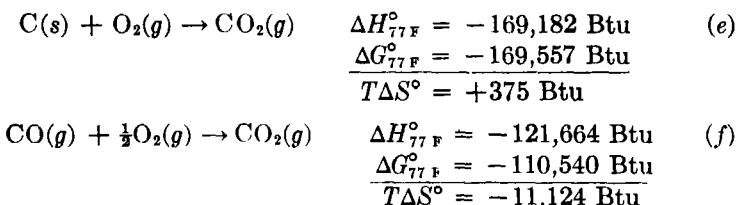
energy change because reactants and products are at unit pressure

$$\Delta G^\circ = -R_0 T \ln K_p \quad (11-19)$$

The degree sign is used to specify the standard state of unit pressure for reactants and products because the free-energy relationships contain the property of entropy, and values of entropy will change markedly with pressure; for this reason the standard states must always be observed (The same convention should also be used for the standard heat of reaction although this value is affected but slightly by changes in pressure, and for ideal gases is unaffected)

Note that Eq (11-19) is a means for evaluating the standard free energy change of a chemical reaction. The partial pressures in the equilibrium mixture can be measured,  $K_p$  computed, and  $\Delta G^\circ$  found by Eq (11-19).

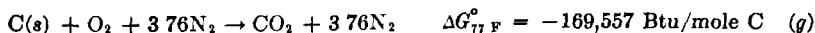
Suppose, now, that the change in the experimentally determined values of free energy<sup>1</sup> and heat of reaction are examined for several reactions



In reaction (e), the change in  $\Delta G^\circ$  is greater than  $\Delta H^\circ$ , and therefore the work that can be obtained from a certain reversible and isothermal process is greater than the negative of the heat of reaction at that same temperature. In reaction (f), however, the opposite situation is present.

**Example 22:** Determine the maximum work that can theoretically be obtained from a flow process for the reaction of pure carbon and atmospheric air at 77° F in the absence of any heat reservoir except the surrounding atmosphere ( $\Delta G_{77^\circ \text{F}}^\circ$  is known to be  $-169,557 \text{ Btu mole}^{-1}$  carbon)

**Solution:** (The word *maximum* has been deliberately used here to impress on the student the futility of determining exactly what the word implies.) The reaction equation is

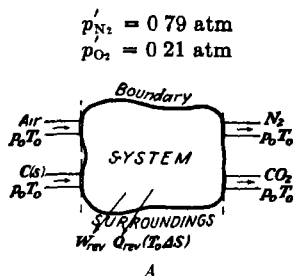


Since  $\Delta G^\circ$  represents the standard free-energy change for the reaction,  $\Delta G^\circ$  is

<sup>1</sup> Values of free energy can be calculated from the values listed in Table XIII (Appendix) for the free energy of formation. The procedure is the same as that followed in Art 11-8

entirely unaffected by the presence of nitrogen because the nitrogen entered and left the system in the same state the change in free energy of the nitrogen is zero

a For the first solution consider Fig A Here it is considered that air enters the system at unit pressure, and for atmospheric air



A

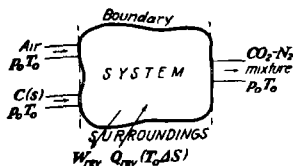
The  $\Delta G$  for Fig A is different from that indicated in Eq (g) because the  $O_2$  and  $N_2$  are not in standard states, and for perfect gases [Eq (11-18)]

$$\begin{aligned} \Delta G &= -nR_0T \ln \frac{p_1}{p_2} \\ \Delta G_{O_2} &= -1.986(537) \ln \frac{0.21}{1} = +1665 \text{ Btu} \\ \Delta G_{N_2} &= -3.76(1.986)(537) \ln \frac{0.79}{1} = +954 \text{ Btu} \\ &\quad \underline{2619 \text{ Btu}} \end{aligned}$$

Since  $G$  is a property,

$$\begin{aligned} \Delta G_{p_1 \text{ to } 1 \text{ atm}} + \Delta G^\circ &= \Delta G_{\text{Fig A}} \\ \Delta G_{\text{Fig A}} &= -169,557 + 2619 = -166,938 \text{ Btu} \\ W_{T \text{ flow}} &= -\Delta G = 166,938 \text{ Btu/mole C} \quad \text{Ans} \end{aligned}$$

Note that the work obtained is now slightly less than the negative of the heat of reaction



B

b The second solution would be to assume the products left as a mixture of  $CO_2$  and  $N_2$  as shown in Fig B For this system

$$\Delta G_{\text{Fig B}} = \Delta G_{O_2(p_{O_2} \text{ to } 1 \text{ atm})} + \Delta G_{N_2(p_{N_2} \text{ to } 1 \text{ atm})} + \Delta G^\circ + \Delta G_{N_2(1 \text{ atm to } p_{N_2})} + \Delta G_{CO_2(1 \text{ atm to } p_{CO_2})}$$

Since the partial pressure of nitrogen in the entering air is the same as the partial pressure in the leaving mixture, these terms cancel For the  $CO_2$

$$\Delta G = -nR_0T \ln \frac{p_1}{p_2} = -1\,986(537) \ln \frac{1}{0.21} = +1665 \text{ Btu}$$

Thus,

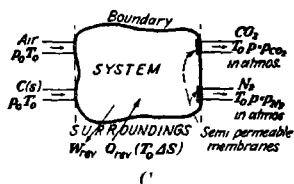
$$\Delta G_{\text{Fig B}} = \Delta G_{\text{O}_2} + \Delta G^\circ + \Delta G_{\text{CO}_2}$$

$$= +1665 - 169,557 - 1665 = -169,557$$

$$W]_{T \text{ flow}} = 169,557 \text{ Btu/mole C} \quad \text{Ans.}$$

This answer is equal to  $-\Delta G^\circ$  because the partial pressures of the  $\text{CO}_2$  and the  $\text{O}_2$  were equal

c A third solution would be to premise that the products leave the system at the partial pressures of these products in the atmosphere. This would seem



to be the most logical assumption. The pressure of  $\text{CO}_2$  in the atmosphere is about

$$p_{\text{CO}_2} = 0.0004 \text{ atm}$$

and  $\Delta G$  for  $\text{CO}_2$  from 1 atm to 0.0004 atm at constant temperature is

$$\Delta G = -nR_0T \ln \frac{p_1}{p_2}$$

$$\Delta G_{\text{CO}_2} = -1\,986(537) \ln \frac{1}{0.0004} = -8360 \text{ Btu}$$

Thus,

$$\Delta G_{\text{Fig C}} = \Delta G_{\text{O}_2} \left( p_{\text{O}_2} \text{ to } 1 \text{ atm} \right) + \Delta G_{\text{N}_2} \left( p_{\text{N}_2} \text{ to } 1 \text{ atm} \right) + \Delta G^\circ + \Delta G_{\text{N}_2} \left( 1 \text{ atm to } p_{\text{N}_2} \right) + \Delta G_{\text{CO}_2} \left( 1 \text{ atm to } p_{\text{CO}_2} \right)$$

$$= +1665 - 169,557 - 8360 = -176,252$$

$$W]_{T \text{ flow}} = -\Delta G = 176,252 \text{ Btu/mole C} \quad \text{Ans}$$

This answer is about 4 per cent higher than  $\Delta G^\circ$

d In deriving Eq (11-9c) the work of expanding the nongaseous phase to its partial pressure was ignored. Investigate the error in this procedure for this example

Equation (11-17) shows for the carbon

$$W]_T = -\Delta G = -\int v dp$$

The density of carbon is approximately  $135 \text{ lb}_m \text{ ft}^{-3}$ , the specific volume per mole is  $0.0885 \text{ ft}^3 \text{ mole}^{-1}$ . Since carbon is relatively incompressible, this value will not change significantly with pressure. The vapor pressure of carbon at 77 F will be considered to be zero, then,

$$-\Delta G = W]_T = -v(\Delta p) = \frac{0.0885(14.7)(144)}{778} = 0.24 \text{ Btu/mole C}$$



Hence, the requirement of unit pressure for the standard state of carbon can be neglected with insignificant error

**11-16. The Third Law of Thermodynamics.** Whenever a chemical reaction occurs, certain properties of the system can no longer be evaluated from an arbitrary datum state. Thus, the heat of reaction, as discussed in Art. 11-5, is the difference between the absolute values of enthalpy (or internal energy) for the products and mixture. The free-energy change  $\Delta G$  for a system that undergoes an isothermal chemical change is also a difference in the absolute values of the properties of products and mixture because  $\Delta G$  includes not only the heat of reaction but also the change in entropy for the system

$$\Delta G]_T = \Delta H - T\Delta S$$

This free-energy change can be evaluated if the value of the equilibrium constant has been experimentally found [Eqs. (11-9) and (11-15) or (11-16)]. However, it could also be evaluated if the absolute entropy of each component in the reaction were known and, also, the heat of reaction. The heat of reaction is readily determined and the absolute entropy can be determined from the principle known as the *Third Law of Thermodynamics*:

**The entropy of a substance becomes zero in a state at the absolute zero of temperature.**

The Third Law enables the absolute entropy of a substance to be calculated from the definition of the change in entropy

$$\begin{aligned} ds &= \frac{dQ}{T} \Big|_{\text{rev}} \\ s - s_0 &= \int_0^T \frac{dQ}{T} \Big|_{\text{rev}} \end{aligned} \quad (5-4)$$

and, by the Third Law, a state exists at the absolute zero where

$$s_0 = 0$$

and therefore, from this state to the temperature  $T$ ,

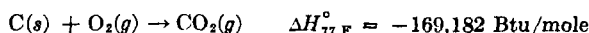
$$s = \int_0^T \frac{dQ}{T} \Big|_{\text{rev}} \quad (11-20)$$

Equation (11-20) can be evaluated if the thermal properties of the substance are known for all temperatures. Of course, the experimental data must be extrapolated to absolute zero because test temperatures will always be above this limiting temperature; this extrapolation is easily accomplished and usually introduces little error.

Tables XIII and XIV (Appendix) list values for the absolute entropies of several substances based upon both experimental and theoretical relationships

**Example 23:** Compute the standard free-energy change for the reaction of Example 22

**Solution:** For this reaction, Table XII (Appendix) shows that



while from Table XIV for the standard state of 77 F and 1 atm pressure

$$s_C^\circ = 1.3609 \text{ Btu/mole R} \quad s_{\text{O}_2}^\circ = 49.003 \text{ Btu/mole R} \quad s_{\text{CO}_2}^\circ = 51.061 \text{ Btu/mole R}$$

By definition

$$\begin{aligned} \Delta G_{537^\circ \text{R}}^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -169,182 - 537(51.061 - 1.3609 - 49.003) \\ &= -169,182 - 374 \\ &= -169,556 \text{ Btu/mole carbon} \quad \text{Ans} \end{aligned}$$

### Problems

1. Write the combustion equation with the theoretical amount of air for acetylene ( $\text{C}_2\text{H}_2$ ) and for decane ( $\text{C}_{10}\text{H}_{22}$ )

2 Repeat Prob 1 but for methyl alcohol ( $\text{CH}_3\text{OH}$ )

3 Repeat Prob 1 but assume that only 85 per cent of the theoretical amount of air is used and that the moles of hydrogen in the products are only one-half the moles of carbon monoxide

4 A fuel oil analyzes 85 per cent carbon and 15 per cent hydrogen (gravimetric) What would be a representative molecular formula?

5 a A coal analysis (gravimetric) is (dry basis)

C	H	O	N	S	Ash	Total
71	4	9	1	3	12	100

Determine the minimum mass of air necessary to obtain complete combustion

b The coal, as fired, had 10 per cent moisture Change the dry analysis in (a) to include the moisture

c Determine the minimum mass of air necessary to obtain complete combustion of the wet coal in (b)

d Compute the sensible heat loss for the products of (b) if the gases leave the furnace at 500 F (Note that the moisture in the coal will increase the amount of water vapor in the products)

6. Repeat Prob 5 but for a coal that analyzes

C	H	O	N	H <sub>2</sub> O	Ash	Total
70	3	2	2	10	13	100

7. The products of combustion of the coal in Prob 6 are analyzed by an Orsat.

CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	Total
14 6	0 2	5 5	79 7	100

a Determine the mass of air burned per pound of coal  
 b Determine the mass of dry products per pound of coal  
 c Assume that the humidity is 0.01 lb<sub>m</sub> of water vapor for each pound of dry air, and determine the amount of water vapor in the products per pound of coal

8. Determine the condensation temperature of the water vapor when dodecane (C<sub>12</sub>H<sub>26</sub>) is burned with the theoretical amount of air at atmospheric pressure. The initial temperature of the air is 60 F and relative humidity is 50 per cent.

9 Octane (C<sub>8</sub>H<sub>18</sub>) and air are burned, and the Orsat products of combustion are

CO <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
9 9	7 2	3 3	0 3	Remainder

Compute the air-fuel ratio by a carbon balance, and compare with the answer found by making a hydrogen balance.

10 The Orsat products of combustion of a hydrocarbon fuel are

CO <sub>2</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>
13 0	2 2	0 2	0 0	0 1

Determine the air-fuel ratio by means of a carbon-hydrogen balance (fuel C<sub>a</sub>H<sub>b</sub>).

11 The Orsat products of combustion of octane and air are

CO <sub>2</sub>	O <sub>2</sub>	CO	Apparent N <sub>2</sub>
8 7	0 2	8 6	Remainder

The measured air-fuel ratio is 11.3 to 1. Compute the air-fuel ratio in the best possible manner.

12 A gas analyzes by volume

CO <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	N <sub>2</sub>	Total
3	19	41	25	9	3	100

Determine the air-fuel ratio for complete combustion and the temperature of condensation of the water vapor in the products (atmospheric pressure).

13. Given the higher heating value of methane (Table XII, Appendix) at constant volume and 77 F, compute the higher and lower heating values at constant pressure and compare with the table values

14 Compute the heat of reaction at constant volume and 77 F of hexadecane for the fuel in the liquid state and all products in the gaseous state

15 Determine the lower heating value of methane at constant volume and at 1000 R

16 Determine the theoretical combustion temperature attained by completely burning methane with 100 per cent excess air at constant volume Assume an initial temperature of 537 R

17 Repeat Prob 16, assuming that combustion occurs at constant pressure

18. For the data of Prob 9, assume that the air used for combustion is at 80 F and 60 per cent relative humidity

a Make a carbon balance and determine the following quantities (for 1 lb<sub>m</sub> of fuel)

1 Mass of water formed by combustion

2 Mass of water in air furnished for combustion

3 Mass of CO in products

4 Mass of H<sub>2</sub> in products

5 Mass of CH<sub>4</sub> in products

6 Mass of CO<sub>2</sub> in products

7 Mass of N<sub>2</sub> in products

b Determine the "heat loss" for the above data, if the gases are at 900 F, in percentage of the heat of reaction at constant pressure (condensed H<sub>2</sub>O in products)

1 Heat loss (sensible) in dry flue gases (Example 4b)

2 Heat loss from incomplete combustion (heat of reaction at constant pressure for each unburned constituent at the temperature of the inlet air 80 F)

CO \_\_\_\_\_ H<sub>2</sub> \_\_\_\_\_ CH<sub>4</sub> \_\_\_\_\_

3 Heat of vaporization of water formed by combustion (80 F)

4 Heat loss in superheating water formed by combustion ( $\Delta H$  of water vapor between 80 and 900 F)

5 Heat loss in superheating water vapor in air ( $\Delta H$  of water vapor, carried in inlet air, between 80 and 900 F)

19. A test of a heat power plant showed the following items Coal, of dry analysis,

C	H	O	N	S	A	Total
76	5	10	1	1	7	100

As fired, the coal contained 10 per cent moisture and had a higher heating value of 12,000 Btu lb<sub>m</sub><sup>-1</sup> The air supplied for combustion was at 70 F and 50 per cent relative humidity The Orsat analysis of the flue gas showed

CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	Total
14	1	4	81	100

The cinder in the ashpit analyzed 45 per cent C. The flue gas entered the stack at 750 F. If the heat transferred to the boiler water is 7500 Btu lb<sub>m</sub><sup>-1</sup> coal as fired, make a heat balance to account for all the energy supplied 12,000 Btu lb<sub>m</sub><sup>-1</sup> coal. (Note Prob. 18 above, a part of the energy supplied cannot be accounted for because it represents heat lost by radiation, etc.)

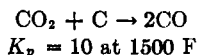
20. If the humidity in the air in Example 19 was neglected, what would be the per cent error?

21. Calculate the degree of dissociation of 1 mole of CO<sub>2</sub> at 5000 R under total pressures of 10 and 100 atm.

22. Repeat Example 21 but for total pressures of 10 and 100 atm.

23. Calculate the degree of dissociation of CO<sub>2</sub> when CO is burned with the theoretical amount of air if the equilibrium temperature is 4000 R and the total pressure is 20 atm.

24. For the reaction



Calculate the maximum conversion possible of CO<sub>2</sub> to CO in the presence of carbon (graphite) at a pressure of  $\frac{1}{2}$  atm and at 1500 F.

25. Determine the minimum work (per pound of air) that is required to separate atmospheric air at 77 F into nitrogen and oxygen each at 1 atm pressure and at 77 F. (Use the reaction box of Art. 11-13 for this separation process.) Explain why the usual process of mixing is an irreversible process. Show that the minimum work is also given directly by Eq. (11-16).

26. Calculate the equilibrium constants for Eqs. (e) and (f) in Art. 11-15 from the data given.

27. Calculate the standard free-energy change for Eq. (f) of Art. 11-15 at 1000 R from the equilibrium constant and, also, by the following steps

$$G_{\text{mixture}}^{1000 \text{ R}} + \Delta G_{\text{mixture}}^{1000 \text{ to } 537 \text{ R}} + \Delta G_{\text{products}}^{537 \text{ R}} = G_{\text{products}}^{537 \text{ R}} \quad (a)$$

$$G_{\text{products}}^{1000 \text{ R}} + \Delta G_{\text{products}}^{1000 \text{ to } 537 \text{ R}} = G_{\text{products}}^{537 \text{ R}} \quad (b)$$

If (a) is subtracted from (b),

$$\Delta G_{1000 \text{ R}}^{1000 \text{ R}} = [G_{\text{products}}^{1000 \text{ R}} - G_{\text{mixture}}^{1000 \text{ R}}] = \Delta G_{537 \text{ R}}^{1000 \text{ R}} + [\Delta G_{\text{mixture}} - \Delta G_{\text{products}}]_{1000 \text{ R}}^{537 \text{ R}}$$

28. Repeat Example 23 but for reaction (f) of Art. 11-15.

29. Calculate the absolute entropy of nitrogen at 500 F and 1 atm pressure (Tables IIB and XIII, Appendix), at 10 atm (assume ideal gas).

30. An automobile engine, using octane as the fuel, has a "thermal" efficiency of 25 per cent, that is, 25 per cent of the higher heating value of the fuel is converted into work. Compute the true efficiency,  $W_{\text{actual}}/W_{\text{maximum}}$ , for this process (Atmospheric temperature is 77 F).

31. A steam power plant contains a thermodynamic cycle with thermal efficiency of 20 per cent, although only 85 per cent of the heat of combustion of the coal is transferred to the cycle. Assuming that coal is pure carbon, determine the true efficiency for the power plant process. (Atmospheric temperature is 77 F.)

## Symbols

$A$	Helmholtz free energy
$AF$	air to fuel mass ratio
$a, b, c, d, e$	unknown numbers, also, moles of components $A, B$ , etc
$c$	heat capacity
$C$	centigrade temperature scale
$F$	Fahrenheit temperature scale
$G$	free energy
$g$	free energy per unit mass (in particular, in the absence of chemical change)
$g$	gas phase
$H$	enthalpy
$h$	specific enthalpy
$K_p$	equilibrium constant
$l$	liquid phase
$n$	moles
$p$	pressure
$p'$	partial pressure in equilibrium mixture
$Q$	heat
$R$	Rankine temperature scale
$R_0$	universal gas constant
$s$	specific entropy, also, solid phase
$S$	entropy
$T$	absolute thermodynamic temperature
$U$	internal energy
$u$	specific internal energy
$V$	volume
$v$	specific volume
$W$	work
$x$	mole fraction, also, unknown number
$y$	unknown number

## Superscripts

$^{\circ}$	(degree)	standard state of 1 atm pressure and specified temperature (usually 77 F)
	(prime)	partial pressure in chemical equilibrium mixture

## Subscripts

$A, B, C, D$	ideal gases
$fg$	change from saturated liquid to saturated vapor
$m$	mass
$p$	constant pressure
$s$	saturated vapor
$T$	constant temperature, usually, for end states
$v$	constant volume
$wg$	watergas

**Suggested References**

- 1 DODGE, B. F.: "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944
- 2 STEINER, L. E.: "Introduction to Chemical Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1941
- 3 LEWIS, G., and M. RANDALL "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923.

**CLASS ASSIGNMENTS**





## CHAPTER XII

### POWER CYCLES—VAPOR

The virtue of reversibility can be exchanged for the virtue of speed by using an irreversible combustion process to create a heat reservoir. Once the heat reservoir has been created, the maximum thermal efficiency that can be obtained from a power cycle is definitely determined (Example 5, Chap. V). In this chapter the power cycle will be examined for irreversibilities, but it should be stressed that the cycle and the heat reservoir must also be examined together, because it is the work obtained from the combination of these two systems that is the all-important factor

**12-1. The Efficiencies of Process and Cycle.** Before the power cycles are investigated, it will be well to define certain performance factors that are in common use. The *thermal efficiency* is a First Law relationship (Art. 3-7), which shows the fractional part of the heat supplied to a cycle that is converted into work

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{Q_A + Q_R}{Q_A} \quad (3-20)$$

However, the thermal efficiency of a cycle does not indicate whether or not the cycle is perfectly performed. A cycle may have a low thermal efficiency and yet be operating in the most efficient manner. For this reason, although high thermal efficiencies are always desirable, other performance factors must also be used to evaluate the cycle fully

When a system undergoes a process, but not a cycle, a *process efficiency* can be formulated to show the accomplishments of the process. The *compression efficiency* (Art. 8-9f) is applied to a pump or compressor and is defined

$$\eta_c = \frac{W_{\text{isentropic}}}{W_{\text{actual}}} \quad (12-1)$$

The *expansion* or *engine efficiency* is applied to a work-producing process:

$$\eta_e = \frac{W_{\text{actual}}}{W_{\text{isentropic}}} \quad (12-2)$$

Equations (12-1) and (12-2) are not restricted to adiabatic processes although the efficiencies can be rationally defended only when the

process is essentially adiabatic, for then Eqs (12-1) and (12-2) merely show the ratio between the actual work and the anticipated ideal work. When properties of the fluid are used in evaluating the work of the process, the actual work required (or delivered) by the real machine will be greater (or less) than the calculated value because of mechanical friction and heat loss (if this latter item has been ignored in the calculations). Thus, Eqs (12-1) and (12-2) can be used to show either "internal" (as in this chapter) or else "over-all" efficiencies.

It is entirely possible for a theoretical power cycle to have a high thermal efficiency even though the real cycle has an extremely low thermal efficiency. A warning of this possibility is given by the *work ratio*, which is defined

$$r_w = \frac{\text{net work from cycle}}{\text{positive work within cycle}} = \frac{\Sigma W}{\Sigma + W} \quad (12-3)$$

For example, suppose the positive work for a theoretical cycle is 10 units and the negative work is 9 units (an unusually low work ratio)

$$r_w = \frac{1}{10}$$

Now suppose that the expansion and compression efficiencies of the real cycle are 0.90, then,

$$\begin{aligned} \text{Output work processes} &= +9 \text{ units} \\ \text{Input work processes} &= -10 \text{ units} \\ \Sigma W &= -1 \text{ unit} \end{aligned}$$

and the real cycle cannot operate as a power cycle because work must be supplied. Moreover, the fixed costs of the installation are high when the work ratio is low. For a cycle with work ratio of 0.1, it would be necessary to buy and install a turbine of 10,000 hp and a compressor of 9,000 hp to produce 1,000 hp.

**12-2. The Carnot Cycle.** One corollary of the Second Law of Thermodynamics is the *Carnot premise*:

**The efficiency of a reversible heat-engine cycle depends only upon the temperatures of source and sink and increases as the source temperature is raised or the sink temperature is lowered.**

To obtain this maximum efficiency, the simplest cycle that can be devised to operate between two heat reservoirs at fixed temperatures is the Carnot cycle (Fig. 12-1). The cycle consists of an isentropic compression *ab*, an isothermal addition of heat *bc*, an isentropic expansion *cd*, and an isothermal rejection of heat *da*, and these reversible

processes may be either flow or nonflow processes. The thermal efficiency of this reversible cycle is

$$\eta_t = \frac{Q_A + Q_R}{Q_A} = \frac{T_A(\Delta s_{bc}) + T_R(-\Delta s_{bc})}{T_A(\Delta s_{bc})}$$

$$\eta_t = \frac{T_A - T_R}{T_A} \quad (5-1b)$$

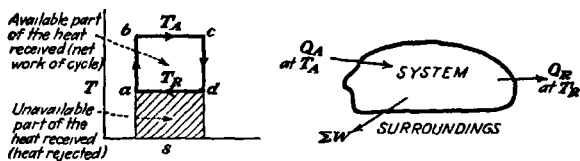


FIG 12-1 The Carnot cycle

Suppose that a vapor, such as steam, is used as the fluid for a Carnot cycle (Fig 12-2). The characteristics of the fluid do not change the thermal efficiency, although now processes  $bc$  and  $da$  are at constant pressure as well as at constant temperature [because, within the two-phase region, temperature and pressure are dependent variables (Art. 6-1)]. If the steam is to undergo a series of nonflow processes, it must be confined in a cylinder by a piston. An essentially adiabatic compression (or expansion) process could be readily accomplished, but the succeeding isothermal process ( $bc$  or  $da$ ) would involve both the addition of heat and the production of work. In practice, it is easier to construct machines that involve only work or only heat because the combination of work and heat in one process requires the machine to be operated at very slow speeds. Consider, too, that the changes in volume throughout the cycle are quite large. For these reasons, a series of flow processes is best used for executing the vapor cycle. In a flow process at constant pressure and temperature, no work is done, therefore, the isothermal processes  $bc$  and  $da$  of Fig 12-1 (which are difficult processes in a nonflow cycle) can be easily approached by using flow processes—a boiler for process  $bc$  and a condenser for process  $da$ .

In the flow system of Fig 12-2, saturated steam  $c$  leaves the boiler, enters the turbine, and expands to state  $d$ . The two-phase mixture at  $d$  then enters the condenser where it is cooled to state  $a$ , and then it enters a compressor where it is compressed to the saturated liquid state  $b$ . The cycle is completed by vaporizing the liquid in the boiler into saturated steam at constant pressure and temperature.

The transfers of heat and work can be found for each flow process

by the First Law equations<sup>1</sup> (which are valid for reversible or irreversible processes)

$$Q = \Delta h \Big|_{\substack{\text{flow, } W=0 \\ \Delta \text{PE, } \Delta \text{KE}=0}} \quad W = -\Delta h \Big|_{\substack{\text{flow, } Q=0 \\ \Delta \text{PE, } \Delta \text{KE}=0}} \quad (3-13)$$

The heat added is

$$Q_A = \Delta h_{bc} \quad (a)$$

The heat rejected is

$$Q_R = \Delta h_{da} \quad (b)$$

The work of the cycle is

$$\Sigma W = Q_A + Q_R = \Delta h_{bc} + \Delta h_{da} = \eta_t Q_A \quad (c)$$

and, also,

$$\begin{aligned} \Sigma W &= W_{ab} + W_{bc} + W_{cd} + W_{da} \\ \Sigma W &= (h_a - h_b) + 0 + (h_c - h_d) + 0 = \Delta h_{bc} + \Delta h_{da} \end{aligned} \quad (d)$$

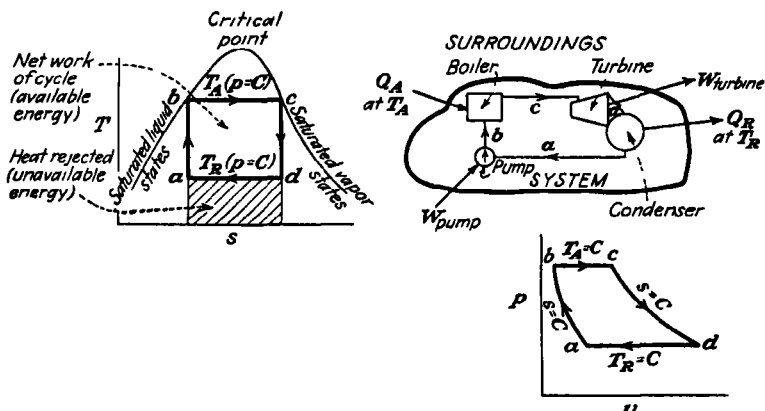


FIG 12-2 The Carnot cycle for a vapor such as steam

Or the Second Law equations can be used since each process is reversible (and these equations are valid for either flow or nonflow processes)

$$Q_{A \text{ rev}} = T_A \Delta s_{bc} = h_{fg}]_{T_A} \quad (e)$$

$$Q_{R \text{ rev}} = -T_R \Delta s_{bc} = T_R \Delta s_{da} \quad (f)$$

$$\Sigma W_{\text{rev}} = \Delta h_{bc} - T_R \Delta s_{bc} \quad (g)$$

Equation (g) evaluates the enclosed area on either the  $pv$  or the  $Ts$  diagram

**Example 1:** Determine the performance factors for the Carnot cycle illustrated in Fig 12-2 if the pressure at  $b$  (and  $c$ ) is 600 psia and the temperature at  $a$  (and  $d$ ) is 60 F. The surrounding temperature is also 60 F (atmospheric)

<sup>1</sup> In the real power cycle, insignificant change occurs in kinetic or potential energy at the boundary for each process, therefore, such changes will be neglected in this chapter

**Solution:** From the Steam Tables for these data,

$p = 600$ psia	$h = 1203.2$	$h_f = 471.6$	$h_{fg} = 731.6$
$t = 486.21$ F	$s = 1.4454$	$s_f = 0.6720$	$s_{fg} = 0.7734$
$p = 0.2563$ psia	$h = 1088.0$	$h_f = 28.06$	$h_{fg} = 1059.9$
$t = 60$ F	$s = 2.0948$	$s_f = 0.0555$	$s_{fg} = 2.0393$

The enthalpy at state  $d$  can be found from the Mollier chart or by calculation.

$$s_c = s_d = s_f + x s_{fg} \quad (6-1)$$

$$1.4454 = 0.0555 + x(2.0393) \quad x_d = 0.6816$$

$$h_d = h_f + x h_{fg} \quad (6-1)$$

$$= 28.06 + 0.6816(1059.9) \quad h_d = 750.5$$

and, in the same manner,

$$x_a = 0.3023$$

$$h_a = 348.5$$

The work for each process is

$$W_{bc} = W_{da} = 0 \quad (\text{constant-pressure flow process})$$

$$W_{cd} = -\Delta h = 1203.2 - 750.5 = 452.7 \text{ Btu/lb}_m$$

$$W_{ab} = -\Delta h = 348.5 - 471.6 = -123.1$$

$$\Sigma W = 329.6 \text{ Btu/lb}_m$$

This answer can be checked by Eq. (g).

$$\Sigma W_{\text{rev}} = \Delta h_{bc} - T_R \Delta s_{bc} = 731.6 - 519.7(0.7734) = 329.7 \text{ Btu/lb}_m$$

With these data

$$\text{Thermal efficiency} = \eta_t = \frac{T_A - T_R}{T_A} = \frac{486.21 - 60}{486.21 + 459.7} = 0.45, \text{ or } 45 \text{ per cent} \quad \text{Ans}$$

$$\text{Compression efficiency} = \eta_c = \frac{W_{\text{isen}}}{W_{\text{act}}} = 1.0, \text{ or } 100 \text{ per cent} \quad \text{Ans}$$

$$\text{Expansion (engine) efficiency} = \eta_e = \frac{W_{\text{act}}}{W_{\text{isen}}} = 1.0, \text{ or } 100 \text{ per cent} \quad \text{Ans}$$

$$\text{Work ratio} = r_w = \frac{\Sigma W}{\Sigma + W} = \frac{329.7}{452.7} = 0.73 \quad \text{Ans}$$

**Example 2:** Upon test of the cycle of Example 1, the expansion and compression efficiencies were found to be 85 per cent, and both processes were essentially adiabatic. Determine the performance factors for these conditions.

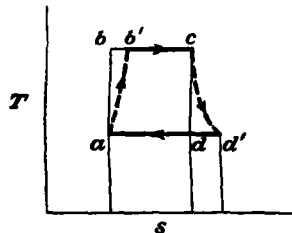


FIG. A

**Solution:** The cycle for this problem is shown in Fig. A. The properties of the fluid at state  $b'$  can be found from Eq. (12-1), and for  $Q = 0$ ,

$$\text{Compression efficiency} = \eta_c = \frac{W_{\text{isen}}}{W_{\text{act}}} = \frac{-\Delta h_{ab}}{-\Delta h_{ab'}} = \frac{-122.6}{-144.2} = 0.85$$

$$h_a - h_{b'} = (W_{\text{act}})_{ab} = -144.2 \text{ Btu/lb}_m$$

$$h_{b'} = h_a + 144.2 = 492.7 \text{ Btu/lb}_m$$

The quality at  $b'$  can be computed

$$h_{b'} = h_f + x h_{fg}$$

$$492.7 = 471.6 + x(731.6)$$

$$x = 0.0289$$

and therefore

$$s_{b'} = 0.6944$$

The properties at state  $d'$  are found from Eq (12-2) for the expansion (engine) efficiency, and with  $Q = 0$ ,

$$\text{Engine efficiency} = \eta_e = \frac{W_{\text{act}}}{W_{\text{isen}}} = \frac{-\Delta h_{cd'}}{-\Delta h_{cd}} = \frac{-452.7}{384.4} = 0.85$$

$$h_c - h_{d'} = (W_{\text{act}})_{cd'} = 384.4 \text{ Btu/lb}_m$$

$$h_{d'} = h_c - 384.4 = 818.8 \text{ Btu/lb}_m$$

and the quality at  $d'$  is

$$h_{d'} = h_f + x h_{fg}$$

$$818.8 = 28.06 + x(1059.9)$$

$$x_{d'} = 0.746$$

$$s_{d'} = 1.5768$$

The heat transferred to the cycle is

$$Q_A = h_a - h_{b'} = 1203.2 - 492.7 = 710.5 \text{ Btu/lb}_m$$

Note that less heat is added in this irreversible cycle than in Example 1 because of the irreversibility in process  $ab'$ . With these data

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{384.4 - 144.2}{710.5} = 0.338, \text{ or } 33.8 \text{ per cent} \quad \text{Ans}$$

$$r_w = \frac{\Sigma W}{\Sigma + W} = \frac{240.2}{384.4} = 0.625 \quad \text{Ans}$$

The Carnot cycle is not used in industry because the vapor-compression process ( $ab$  in Fig. 12-1 or 12-2) cannot be efficiently accomplished, and therefore the practical system would have a low thermal efficiency and a high cost

**12-3. The Rankine Cycle.** A cycle with a higher work ratio, but with a lower thermal efficiency than the Carnot cycle, is obtained by substituting a liquid-compression process for the work-consuming vapor-compression process. Thus, in Fig 12-3, the Carnot cycle is modified into a *Rankine* cycle by completing the condensation process in the condenser and then reversibly pumping the saturated liquid at state  $a$  to the boiler pressure at state  $b$ . Heat is added at constantly increasing temperatures from  $b$  to  $c$ , and at constant temperature from

$c$  to  $d$ , in a reversible,<sup>1</sup> constant-pressure process. The fluid is reversibly expanded in a turbine from state  $d$  to state  $e$ , and the reversible heat-rejection process of condensation  $ea$  at constant temperature and pressure completes the cycle

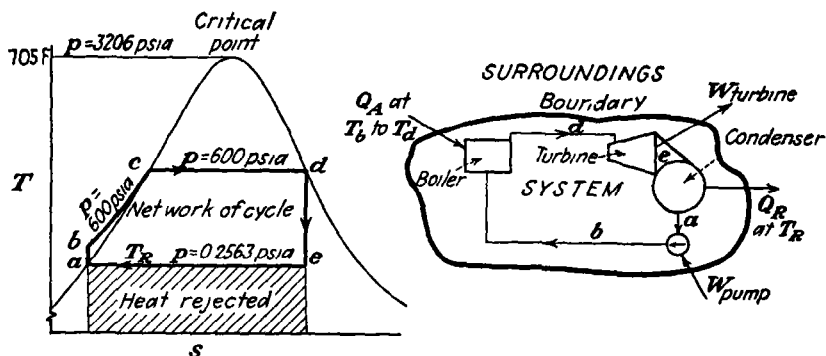


FIG 12-3. The Rankine cycle (temperature rise  $ab$  greatly exaggerated)

In the same manner as for the Carnot cycle, the relationships for the Rankine cycle are found to be

$$Q_A = \Delta h_{bd} = h_d - h_b \quad (a)$$

$$Q_R = \Delta h_{ea} = h_a - h_e \quad (b)$$

$$\Sigma W = Q_A + Q_R = \eta_i Q_A \quad (c)$$

$$\Sigma W_{rev} = \Delta h_{bd} - T_R \Delta s_{bd} \quad (d)$$

$$\eta_i = \frac{\Sigma W}{Q_A} \quad (3-20)$$

**Example 3:** For the same conditions as in Example 1, determine the performance factors for the Rankine cycle of Fig 12-3

**Solution:** The pump work for the liquid is closely (Example 7, Chap. VI)

$$W = -v\Delta p$$

and at  $t = 60$  F, for saturated water,  $v_f = 0.01604$  ft<sup>3</sup>/lb<sub>m</sub>,

$$W = - \frac{0.01604(600 - 0.2563)144}{778.16} = -1.78 \text{ Btu/lb}_m$$

The properties at each state are (Steam Tables and Example 1)

$h_a = 28.06$	$h_b = 29.84$	$h_d = 1203.2$	$h_e = 750.5$
$s_a = 0.0555$	$s_b = 0.0555$	$s_d = 1.4454$	$s_e = 1.4454$

<sup>1</sup> The irreversibility caused by a temperature difference between cycle and heat reservoir can be disregarded here by defining the boundary of the system so that the temperature difference is in the surroundings (Art 4-3). The loss of available energy because of the temperature difference is thus not debited against the cycle (Art 12-10 and Example 7)



Then,

$$\begin{aligned} Q_A &= h_d - h_b = 1173.4 \text{ Btu/lb}_m \\ Q_R &= h_a - h_{a'} = -722.4 \text{ Btu/lb}_m \\ \Sigma W &= 451.0 \text{ Btu/lb}_m \\ W_{\text{turbine}} &= h_d - h_{d'} = 452.7 \text{ Btu/lb}_m \\ W_{\text{pump}} &= h_a - h_b = -1.78 \text{ Btu/lb}_m \end{aligned}$$

With these data,

$$\eta_1 = \frac{\Sigma W}{Q_A} = \frac{451.0}{1173.4} = 0.384, \text{ or } 38.4 \text{ per cent} \quad \text{Ans}$$

Compression and expansion efficiencies are 100 per cent Ans

$$r_w = \frac{\Sigma W}{\Sigma + W} = \frac{451}{452.7} = 0.996 \quad \text{Ans}$$

**Example 4:** Upon test of the cycle of Example 3, the expansion and compression efficiencies are found to be 85 per cent, and both processes were essentially adiabatic. Determine the performance factors for these conditions.

**Solution:** For a compression efficiency of 85 per cent, the actual pump work will be

$$\frac{W_{\text{isen}}}{W_{\text{act}}} = \frac{-1.78}{W_{\text{act}}} = 0.85 \quad W_{\text{act}} = -2.09 \text{ Btu/lb}_m$$

Since the real process is adiabatic, the enthalpy of the fluid is increased by 2.09 Btu/lb<sub>m</sub>. The entropy increase during this irreversible process can be approxi-

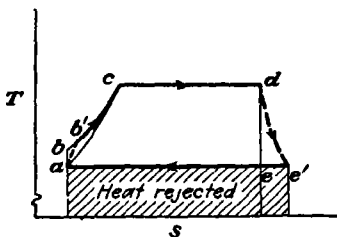


FIG B

mately determined by noting that the work, in excess of the reversible work, is dissipated in turbulence and friction with a net effect equivalent to a transfer of heat to the fluid

$$\Delta s_{ab} \approx \frac{2.09 - 1.78}{60 + 459.7} = \frac{0.31}{519.7} = 0.0006 \text{ Btu/lb}_m \text{ R}$$

The properties at each state in Fig B are (Steam Tables, Examples 1 and 2).

$$\begin{array}{llll} h_a = 28.06 & h_{b'} = 30.15 & h_d = 1203.2 & h_{d'} = 818.4 \\ s_a = 0.0555 & s_{b'} = 0.0561 & s_d = 1.4454 & s_{d'} = 1.576 \end{array}$$

Then,

$$\begin{aligned} Q_A &= h_d - h_{b'} = 1173.0 \\ Q_R &= h_a - h_{d'} = -790.3 \\ \Sigma W &= 382.7 \text{ Btu/lb}_m \\ W_{\text{turbine}} &= h_d - h_{d'} = 384.8 \\ W_{\text{pump}} &= h_a - h_{b'} = -2.1 \\ \Sigma W &= 382.7 \text{ Btu/lb}_m \end{aligned}$$

With these data,

$$\eta = \frac{\Sigma W}{Q_A} = \frac{382.7}{1173.0} = 0.326, \text{ or } 32.6 \text{ per cent} \quad \text{Ans}$$

$$r_w = \frac{\Sigma W}{\Sigma + W} = \frac{382.7}{384.8} = 0.995 \quad \text{Ans}$$

The answers for Examples 1, 2, 3, and 4 can be compared

	Example 1 Theoretical Carnot	Example 2 Practical A	Example 3 Theoretical Rankine	Example 4 Practical B
Thermal efficiency	45 %	33.8 %	38.4 %	32.6 %
Work ratio	0.73	0.625	0.996	0.995

This table shows that the Rankine cycle can be more readily approached by the real cycle *B* than if the Carnot cycle were to be attempted (cycle *A*). Too, the work ratio of cycle *B* is not perceptibly different from the work ratio of the Rankine cycle and is much higher than that of cycle *A*. Note that the efficiency of cycle *A* is only 1.2 per cent greater than the efficiency of cycle *B* although the Carnot cycle is 6.6 per cent more efficient than the Rankine cycle.

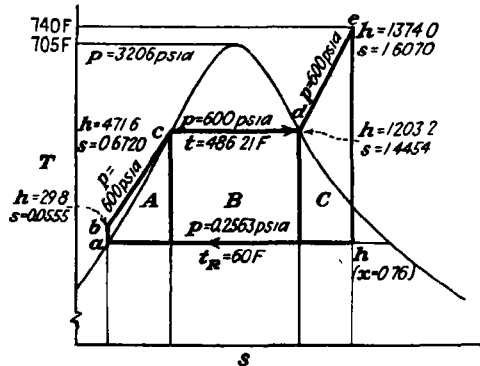


FIG 12-4 The Rankine cycle with superheated steam (temperature rise *ab* greatly exaggerated)

The foregoing examples indicate that, although the Carnot cycle is theoretically most desirable, practically the Rankine cycle is less sensitive to irreversibilities that are always present in real cycles. Since the net work of the Carnot cycle is low and, therefore, equipment size and cost high, it becomes evident that improvements in the Rankine cycle are the most logical fields to explore.

The thermal efficiency of any cycle can be increased by increasing the temperature of the heat-addition process. But for water, as is evident in Fig 12-3, the increase in temperature is accompanied by a considerable increase in pressure. (In fact, for a temperature of

705 F—the critical temperature—the critical pressure is 3,206 psia ) Because of this, steam must be superheated if the highest possible temperature is to be attained in the cycle. In Fig 12-4 is shown a Rankine cycle that uses steam superheated to 740 F (the name *Rankine cycle* does not limit the state of the steam). This cycle can be analyzed in the same manner as illustrated in Examples 1 and 3. However, it is instructive to consider the cycle to be made up of three independent cycles, *A*, *B*, and *C*. Cycle *A* is the cycle added to the Carnot cycle *B* to eliminate the vapor-compression process. Cycle *C* can be called the superheat cycle. Then for these cycles:

	1		2	3	4
	Heat added		Heat rejected	Work (1) + (2)	Thermal efficiency, % (3) - (1)
	Btu	% of Total			
Cycle <i>A</i>	$h_c - h_b$ 441.8	32.8	$-T_R(s_c - s_i)$ -320.4	121.4	27.5
Cycle <i>B</i>	$h_d - h_c$ 731.6	54.5	$-T_R(s_d - s_c)$ -401.9	329.7	45.1
Cycle <i>C</i>	$h_e - h_d$ 170.8	12.7	$-T_R(s_e - s_d)$ -84.0	86.8	50.8
	$\Sigma Q_A = 1344.2$	100.0	$Q_R = -806.3$	$\Sigma W = 537.9$	

$$\eta_t = \frac{\Sigma W}{\Sigma Q_A} = 0.400 \text{ or } 40.0 \text{ per cent}$$

The tabled values reveal, quite clearly, that cycle *A*, wherein water is heated from the lowest temperature to the saturation temperature, has a particularly low thermal efficiency that exerts a strong influence on the over-all efficiency because of the relatively large amount of heat added. Cycle *C* does not radically affect the over-all thermal efficiency (or the efficiency of the Carnot cycle *B*) because the superheat accounts for only 12.7 per cent of the total heat transferred to the system. This analysis indicates that the properties of water are not particularly suited to the prime requirement for maximum thermal efficiency: heat to be transferred to the cycle at the highest possible temperature.

An advantage of superheat, not shown by a theoretical analysis, is the elimination, in part, of moisture from the steam in the last stages of the expansion in the turbine. Note that increasing the pressure<sup>1</sup>

<sup>1</sup> Most modern large central stations are designed for 800 to 900 psia, 900 to

of the Rankine cycle and so increasing the temperature of heat addition also cause the final condition of the steam to become increasingly wet (Fig 12-3) The presence of over 10 per cent moisture in the steam will cause quite serious erosion of the turbine blades and, also, a decreased engine efficiency; these conditions can be corrected by superheating the steam

**12-4. The Ideal Fluid for the Rankine Cycle.** In view of the disclosures in Art 12-3, a digression will be made here to consider the properties of an ideal fluid The ideal fluid for the Rankine cycle, and therefore the ideal fluid for the industrial power plant, should have the following properties:

- 1 The latent heat of vaporization should be large and the heat capacity of the liquid should be small [at least relative to each other, for then the effect of cycle *A* (Fig 12-4) on cycle *B* would be negligible and the efficiency of the Rankine cycle (cycles *A* + *B*) would be essentially that of the Carnot cycle *B*]
- 2 The critical point should be above the highest operating temperature [This would allow the temperature of heat addition to cycle *B* (Fig 12-4) to be increased to the highest possible value that the material can withstand]
- 3 The vapor pressure, at the highest operating temperature, should not be high (High pressures not only are dangerous but also increase design costs and maintenance problems)
- 4 The vapor pressure, at the lowest operating temperature, should be higher than atmospheric pressure (This would prevent air from leaking into the condenser,<sup>1</sup> thus raising the mixture pres-

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925 F operation, although pressures of 1,500 psia are not uncommon Smaller industrial plants use pressures of 300 to 600 psia and temperatures of 450 to 750 F

<sup>1</sup>In an idle steam power plant, the condenser contains air at atmospheric pressure When the turbine is started, steam can expand only to the condenser pressure, and this will be atmospheric pressure An air vent on the condenser is connected to an air pump, and the air (and its contained steam vapor) is pumped from the condenser The exhaust steam from the turbine, on condensing upon the cold condenser tubes, suffers a tremendous contraction of volume, and therefore the pressure falls The pressure continues to fall until all the air is removed, then, the pressure in the condenser will be that dictated by the vapor pressure of the condensate This pressure is controlled by the temperature of the cooling-water supply For example, when steam condenses, a high vacuum exists at the normal temperature of the coolant at 60 F the saturation pressure of steam is 0.2563 psia Thus, the air pump must be kept in continuous operation to remove air that leaks into the high vacuum system, and this pump work is an added cost of operation Note, especially, that the steam from the turbine can only expand

sure, which is the pressure of exhaust for the turbine and therefore controls the work output to a great extent )

- 5 The entropy of the saturated vapor should not change markedly with change of pressure; this would require the locus of saturated-vapor states on the temperature-entropy diagram to be steep [However, it should not be at such an angle that the steam is in the superheat region as it enters the condenser, for then the steam has not expanded to the lowest possible temperature, the condensation temperature at the exhaust pressure. Too, the rate of heat transfer is higher for wet steam than for superheated steam. But neither should the steam, in passing through the turbine, become too wet (more than 10 per cent moisture); else erosion of the turbine blades and reduced blading efficiency will become problems.]
- 6 The properties of the fluid should be conducive to high rates of heat transfer in order that both surface areas and temperature

differences can be small in the heat exchanger.

- 7 The fluid should be cheap in cost, stable, nonexplosive, and noncorrosive under all conditions of operation, and nonpoisonous for safety of personnel

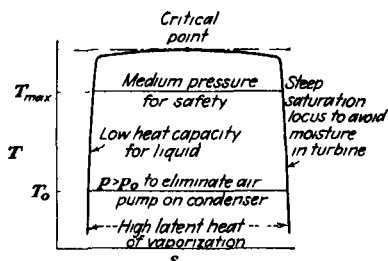


FIG 12-5 The characteristics of an ideal fluid for the Rankine cycle

No fluid is known that satisfies all these desirable characteristics, which are illustrated, in part, by

Fig 12-5 Water, of course, is the usual fluid for the power cycle because it is cheap and plentiful. The problem, then, is either to discover a perfect fluid or else to adapt the Rankine cycle to the properties of water in order to obtain the highest possible thermal efficiency

to the mixture pressure in the condenser, hence, the presence of air prevents the attainment of the maximum work

Although this argument is based upon pressure, it should be remembered that pressure is only the incidental factor in obtaining the maximum work. The prime essential is to operate the cycle between the highest and the lowest possible temperatures. But the attainment of the lowest temperature is also reflected by the attainment of a definite pressure, which is dictated by the pressure-temperature characteristics of the fluid. Therefore, fluids, such as steam, which have low vapor pressures at atmospheric temperatures, are undesirable because leakage of air into the system will prevent expansion to the pressure dictated by the lowest possible temperature.

**12-5. The Reheat Cycle.** It should now be evident that raising the average temperature of heat additions to the water in a Rankine cycle requires not only superheat but also a high pressure, which causes an excessive increase in the moisture content of the steam in the expansion process through the turbine. This fault can be corrected by the *reheat cycle* (Fig 12-6), which is a modification of the Rankine cycle. Here steam is expanded in a turbine to an intermediate pressure ( $h$ ) where the moisture content is not excessive. The steam is piped back to the furnace, reheated to the initial temperature (process  $h_i$ ), and then expanded in a second turbine to the condenser temperature (process  $ij$ ). Inspection of Fig 12-6 shows that expansion within the two-phase region has been decreased by the reheat

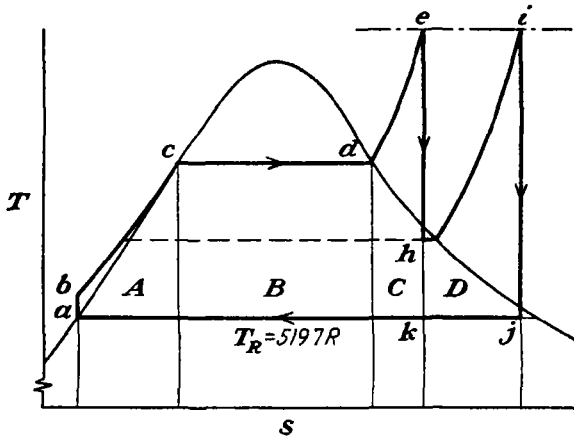


FIG 12-6 The reheat cycle (temperature rise  $ab$  greatly exaggerated)

Whether or not the reheat cycle will have a greater efficiency than the Rankine cycle can be visualized by means of Fig 12-6. Note that the reheat cycle can be considered to be made up of cycles  $A$ ,  $B$ ,  $C$ , and  $D$ . Hence, reheating the steam will increase the thermal efficiency only if the efficiency of cycle  $D$  is greater than the efficiency of the Rankine cycle ( $A + B + C$ ). The thermal efficiency of cycle  $D$  depends directly upon the temperature of point  $h$ . If the temperature of  $h$  is close to the temperature of  $d$ , then reheating will raise the thermal efficiency of cycle  $ABCD$  above that of cycle  $ABC$ . If reheating is delayed until the expansion has proceeded to the neighborhood of point  $k$ , then cycle  $D$  may have a low thermal efficiency, and the combined efficiency of cycle  $ABCD$  may be less than the efficiency of the Rankine cycle  $ABC$ .

**Example 5:** For the data of Art. 12-3 and Fig. 12-4, assume that steam expands in a high-pressure turbine to the saturated-vapor state. The steam is reheated to the initial temperature (740 F) and then expanded in a low-pressure turbine to the condenser temperature (60 F). Determine the efficiency of the cycle.

**Solution:** Since expansion in the high-pressure turbine is to the saturated state ( $h$  in Fig. 12-6 is to be on the saturated-vapor line), either a Mollier chart or Table 1 of the Steam Tables shows

Given  $s_h = 1.6070$  (saturated vapor)  
 Read  $p_h = 94.8$  psia  $t_h = 324$  F  $h_h = 1186.2$

The steam is reheated at constant pressure to the original temperature, 740 F. The properties at this state are

$p_1 = 94.8$  psia  $h_1 = 1399.5$   $s_1 = 1.8265$

and the efficiency of cycle  $D$  is found

Heat added	Heat rejected	$\Sigma$ Work	Thermal efficiency of cycle $D$
$h_1 - h_h$ 213.3	$-T_R(s_1 - s_h)$ -114.1	99.2	46.5%

The efficiency of the combined cycles is obtained by adding the heat and work quantities found above to the values for the Rankine cycle in Art. 12-3

$$\begin{array}{rcl}
 Q_A = 1344.2 & \Sigma W = 537.9 & \text{Art. 12-3} \\
 Q_A = 213.3 & \Sigma W = 99.2 & \text{cycle } D \\
 \hline
 Q_A = 1557.5 & \Sigma W = 637.1 & \text{cycle } ABCD \\
 \eta = \frac{\Sigma W}{Q_A} = \frac{637.1}{1557.5} = 0.409, \text{ or } 40.9 \text{ per cent} & \text{Ans} &
 \end{array}$$

Thus a gain in thermal efficiency of only 0.9 per cent has been achieved.

The work obtained from each turbine is not shown by this method. If this information is desired,

$$\begin{array}{rcl}
 W_{HP} = (h_e - h_h)_{s=c} = 1374.0 - 1186.2 = 187.8 \text{ Btu/lb}_m & \text{Ans} \\
 W_{LP} = (h_1 - h_i)_{s=c} = 1399.5 - 948.0 = 451.5 \text{ Btu/lb}_m & \text{Ans} \\
 \Sigma = 639.3 & &
 \end{array}$$

(From this quantity must be subtracted the pump work if the net work of the cycle is to be obtained.)

Although reheat can be employed as a means for raising the thermal efficiency of a cycle, the thermodynamic gain is small, and therefore the main purpose of the reheat is to eliminate erosion caused by moisture. Because of this, reheating is used when high operating pressures cause a high percentage of moisture to appear in the expansion process. Not only is erosion relieved, but also the engine effi-

ciency of the turbine is increased by the decrease in moisture. Accompanying these advantages, however, are the disadvantages caused by the increased cost and complexity of the system. Since the steam to be reheated is at low pressure, the volume is large and the friction losses are high in transporting the steam to the reheater in the furnace and then back again to the low-pressure turbine. For these reasons, increasing the superheat, without reheating, may be an easier but less effective means of approaching the same end point.

**12-6. The Regenerative Cycle.** The thermal efficiency of the Rankine cycle is less than that of the Carnot cycle because heat is added at other than the highest temperature. But this deficiency can be eliminated by *regenerative heating* although the method to be first discussed is highly impractical. In Fig 12-7, the condensate is

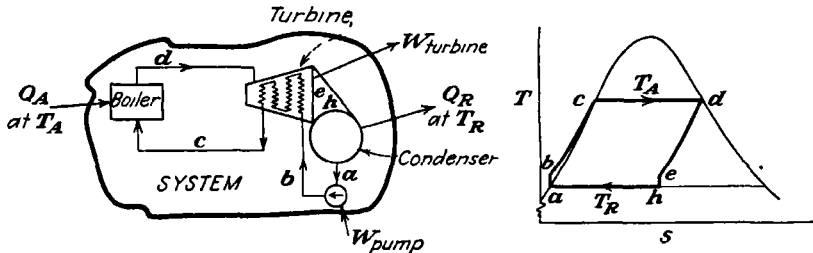


FIG 12-7 A theoretical regenerative cycle (temperature change  $ab$  and, therefore,  $eh$  greatly exaggerated)

pumped to boiler pressure and then led through heat-transfer coils installed in the turbine. By this method, the fluid can be conceived to be reversibly raised in temperature from  $b$  to  $c$ , while the expanding fluid can be conceived to be reversibly cooled from  $d$  to  $e$ . The thermal efficiency of this *regenerative cycle* is the Carnot efficiency. The proof of this statement is contained in the following three conditions (1) Heat is added to the cycle at one constant temperature  $T_A$ . (2) Heat is rejected from the cycle at another constant temperature  $T_R$ . (3) All processes are (or can be conceived to be) reversible. Then, by the reasoning in Art 5-3, the efficiency of this reversible cycle is equal to that of a Carnot cycle, which employs the same two heat reservoirs.

However, even if such a regenerative turbine could be constructed, it would be undesirable for fluids such as water, because the moisture content of the expanding steam in the turbine would be increased by the cooling. An alternative method can be proposed. In Fig 12-8a is shown a regenerative system wherein a small fraction  $y$  of the steam is extracted from the turbine before it has completely expanded to the



**final temperature** The extracted steam is mixed with the feed water in an "open" heater<sup>1</sup> In this manner the temperature of the water can be increased (from  $b$  to  $c$ ) by condensing the extracted steam (from  $i$  to  $c$ ) without changing the quality of the steam within the turbine. With an infinite number of extraction points, each at a different temperature of the expansion, and an infinite number of heaters, the temperature difference between the extracted steam and the feed water will be made infinitely small and the irreversibility of mixing will be similarly decreased For this hypothetical system, heat will be transferred only at the highest and lowest temperatures

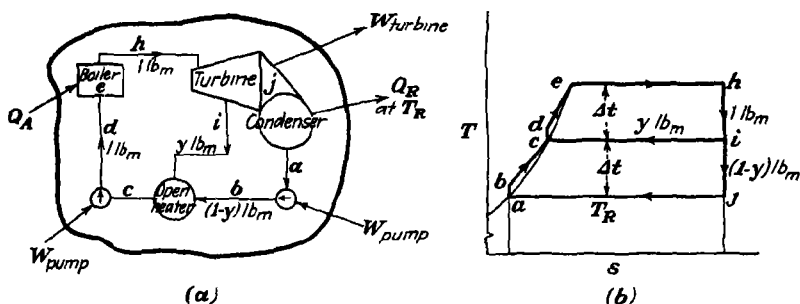


FIG 12-8 The regenerative (extraction) system (temperature rise in pumps greatly exaggerated)

that are experienced by the system With a finite number of extraction points, the irreversibility of each mixing process is a loss in available energy Despite this loss, the thermal efficiency of the irreversible regenerative "cycle" can be greater than the thermal efficiency of the reversible Rankine cycle This is so because heat is added at a higher average temperature in the regenerative system, and therefore a greater percentage of this heat can be converted into work The proof of this statement is best shown by an illustrative example (Example 6)

The temperature-entropy diagram for the fluid in a one-heater regenerative system is constructed in the usual manner for 1 lb<sub>m</sub> of fluid, and the actual quantity of fluid present in each process is shown on the diagram (Fig 12-8b) Note that the quantities of steam  $y$  and  $(1 - y)$  undergo different cycles The path  $abcdehija$  is followed by the fraction  $(1 - y)$ ; the path  $cdehic$  is followed by the fraction  $y$ .

<sup>1</sup> An open heater is a mixing or direct-contact heater In a closed heater, the hot and cold fluids are separated, heat being transferred through metal coils (Fig 12-9)

Thus, the name regenerative cycle is not precisely correct because a combination of cycles is present; usage, however, justifies the name. In other words, the irreversible regenerative system, itself, cannot be shown on the  $Ts$  diagram, but the paths followed by each portion of the fluid in the real system can be accurately portrayed. However, because of the irreversibilities, proper interpretation must be made as to which of the areas on the diagram represent transfers of heat to the system. The heat added to the system is

$$Q_A = h_h - h_d \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

The heat rejected from the system involves only the fraction  $(1 - y)$ .

$$Q_R = (1 - y)(h_a - h_i) \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

The work done in processes  $hi$  and  $cd$  is

$$W_{hi} = (h_h - h_i) \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

$$W_{cd} = (h_c - h_d) \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

Processes  $ij$  and  $ab$  involve only the fraction

$$(1 - y) \frac{\text{lb}_m}{\text{lb}_m \text{ water through boiler}}$$

and the work is

$$W_{ij} = (1 - y)(h_i - h_j) \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

$$W_{ab} = (1 - y)(h_a - h_b) \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

(Note that the units for all of these quantities are identical.)

The expansion process in the real turbine will be irreversible and essentially adiabatic. Thus the engine efficiency of a simple *regenerative*<sup>1</sup> turbine equals

$$\eta_e = \frac{y(h_h - h_{i'}) + (1 - y)(h_h - h_{i'})}{[y(h_h - h_{i'}) + (1 - y)(h_h - h_{i'})]_{s-c}}$$

where  $h_{i'}$  = enthalpy at extraction point

$h_{i'}$  = enthalpy at turbine exit

<sup>1</sup> If the extracted steam is used for purposes other than to heat the condensate, the turbine is called an *extraction turbine*.

For a finite number of heaters, the irreversibility of mixing can be held to a minimum by dividing the temperature rise equally among the heaters. Thus, in Fig. 12-8 the cold water at  $b$  could be pumped into a boiler and the temperature difference  $be$  would exist between the cold water and the boiler water. This irreversibility is cut in half by using one extraction heater to raise the temperature from  $b$  to  $c$  before the water enters the boiler. (In effect the boiler acts as a heater to raise the temperature from  $d$  to  $e$ ) If two heaters are used, the temperature rise from  $b$  to  $e$  is divided into three parts, one part for each heater, and the third part for the boiler. (Even if the cycle is a superheat cycle, the same reasoning is valid. The temperature rise from condenser to boiler is divided into equal increments without regard for the temperature of superheat.)

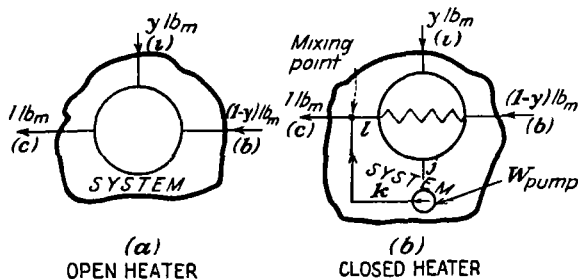


FIG 12-9 Feedwater heaters

The amount of steam that must be extracted for each heater is readily found from the First Law. The heater in Fig 12-8 can be arbitrarily enclosed by a boundary to form a new system (Fig 12-9a). For this flow system, which is essentially adiabatic,

$$Q - W = \Delta h$$

and

$$Q = 0 \quad W = 0$$

Therefore,

$$\Sigma \Delta h = 0$$

$$h_c = yh_i + (1 - y)h_b$$

$$y = \frac{h_c - h_b}{h_i - h_b}$$

Note that, if two or more heaters are used, each heater can be considered to be an independent system and analyzed in the same manner as shown here. The heater closest to the boiler must be first analyzed, or else there will be more than one unknown.

In commercial applications, *closed* heaters, such as that illustrated in Fig. 12-9b, are more usually encountered. Here the feed water is passed through coils in the heater and not directly mixed with the extracted steam, although the condensate from the extracted steam is pumped into the feed-water line, as shown in Fig. 12-9b. For the system of Fig. 12-9b, the First Law can be applied:

$$Q - W = \Delta h \quad \text{and} \quad Q = 0$$

and

$$\begin{aligned} -W &= h_c - yh_i - (1 - y)h_b \\ y &= \frac{h_c - h_b + W}{h_i - h_b} \end{aligned}$$

(In this equation, note that the value substituted for  $W$  will be negative, by convention.) In the actual installation the saturation temperature  $t_s$  of the extracted steam is hotter than the temperature  $t_i$  of the leaving feedwater, and this *terminal difference* may range in value from 5 to 20°.

**Example 6:** A Rankine cycle operates with steam between the limits of 600 psia, 740 F and 60 F (The same data were used in Art 12-3 for the superheated Rankine cycle) Determine the thermal efficiency if a heater is installed to heat the feed water in the manner illustrated in Fig 12-8

**Solution:** The optimum extraction pressure for the heater is first determined.

$$\begin{aligned} p &= 600 \text{ psia} & t_s &= 486.21 \text{ F} \\ & & t_b &= 60 \text{ F} \\ & & 546.21 \div 2 &= 273.1 \text{ F} \end{aligned}$$

The pressure corresponding to this temperature is 44 psia. The properties at different states throughout the cycle are shown in Fig C (Mollier chart and Steam Table values)

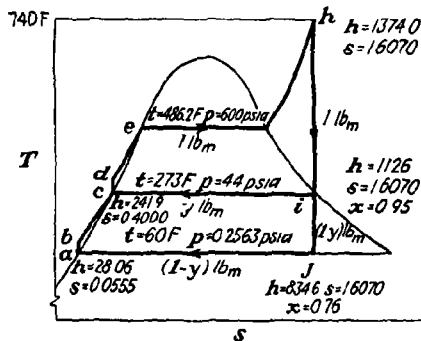


FIG C

The enthalpies at states *b* and *d* are calculated.

$$h_d = h_c + v\Delta p \\ = 241.9 + \frac{0.0172(800 - 44)144}{778.16} = 241.95 + 1.77 = 243.72 \text{ Btu/lb}_m$$

$$h_b = h_a + v\Delta p \\ = 28.06 + \frac{0.0160(44 - 0.25)144}{778.16} = 28.06 + 0.13 = 28.19 \text{ Btu/lb}_m$$

The fraction of extracted steam is calculated

$$y = \frac{h_c - h_b}{h_s - h_b} \\ y = \frac{241.95 - 28.19}{1126 - 28.19} = 0.195$$

The heat added is equal to

$$Q_A = (h_b - h_d) = 1374 - 243.7 = 1130.3 \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

The heat rejected is equal to

$$Q_R = (h_a - h_j)(1 - y) = (28.06 - 834.6)(0.805) \\ = -649.3 \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

and the thermal efficiency is

$$\eta_t = \frac{Q_A + Q_R}{Q_A} = \frac{481.0}{1130.3} = 0.426, \text{ or } 42.6 \text{ per cent} \quad \text{Ans}$$

Compare this with the superheated Rankine cycle efficiency, 40.0 per cent

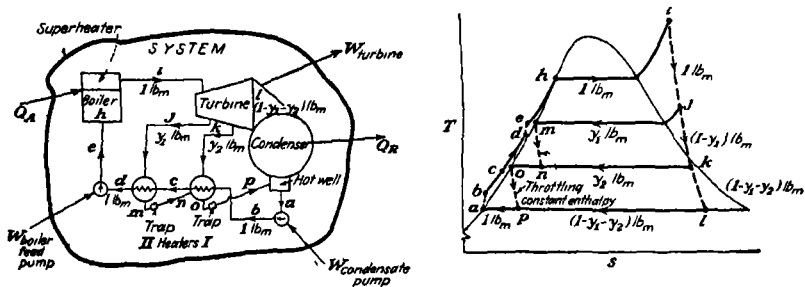


Fig 12-10 A two-heater regenerative system (terminal differences and temperature rise in pumps greatly exaggerated)

Figure 12-10 illustrates a two-heater system, which does not require auxiliary pumps because the condensate of the extracted steam is "flashed" or "cascaded" back to a low-pressure region. Here the fraction  $(1 - y_1 - y_2)$  passes through the cycle  $abcdehijkla$ ; the fraction  $y_1$  passes through the cycle  $abcdehijmnpa$ , the fraction  $y_2$  passes through the cycle  $abcdehijkopa$ . For this system

$$Q_A = h_i - h_e \frac{\text{Btu}}{\text{lb}_m \text{ water through boiler}}$$

$$Q_R = (h_a - h_i)(1 - y_1 - y_2) + (h_a - h_p)(y_1 + y_2)$$

$$W_{\text{turbine}} = (h_i - h_j) + (h_j - h_k)(1 - y_1) + (h_k - h_l)(1 - y_1 - y_2)$$

or

$$W_{\text{turbine}} = (h_i - h_l)(1 - y_1 - y_2) + (h_i - h_j)y_1 + (h_i - h_k)y_2$$

Note that the terminal difference for heater 1 is  $(t_o - t_c)$ ; for heater 2 it is  $(t_m - t_d)$

In some instances the extracted steam is used for process work other than to warm the feed water. A system of this type can be called an *extraction system* but not a *regenerative system*.

**12-7. The Binary-vapor System.** The discussion in previous articles has indicated that an ideal fluid and a Rankine cycle would offer the best practical solution to the problem of converting heat into work. In the absence of an ideal fluid, the Rankine cycle can be modified into a regenerative cycle, but here the low critical temperature of water mitigates against adding all the heat at the highest possible temperature. This disadvantage of water for high-temperature operation can be overcome, in part, by "topping" the regenerative cycle with a cycle that uses a fluid with a higher critical temperature than that of water and, also, a lower heat capacity for the liquid phase. Thus, in Fig 12-11, a *binary-vapor* system is illustrated, consisting of a regenerative cycle, which uses water as the fluid, and a Rankine cycle, which uses mercury as the fluid.

The properties of mercury (Table V, Appendix) are such that the pressure is only 180 psia for a vaporization temperature of 1000 F. Since the heat capacity of the liquid is small, a regenerative cycle is not demanded,<sup>1</sup> and the simple Rankine cycle can be used. Heat is transferred to the mercury cycle to heat the liquid at state *l* to the saturated vapor state *m*. The mercury vapor then expands in a turbine to the temperature *n* with corresponding pressure of 2 psia. (Unfortunately, expansion cannot be made to 60 F because the vacuum in the mercury condenser would be extremely high and therefore impractical to maintain.) Condensation of the mercury takes place in a condenser that is also a boiler for the water cycle. The mercury is pumped back into the mercury boiler to complete the cycle.

The bottom fluid of the system passes through the processes dictated by the extraction cycle. Here heat is added to superheat the

<sup>1</sup> A regenerative cycle would be undesirable because the efficiency of the furnace would be decreased (Art 12-9)

steam and so decrease the moisture content in the final stages of expansion

However, the mercury cycle must maintain a greater mass flow rate than the steam cycle since the latent heat of vaporization of steam is considerably greater than that of mercury. The relative flow rates

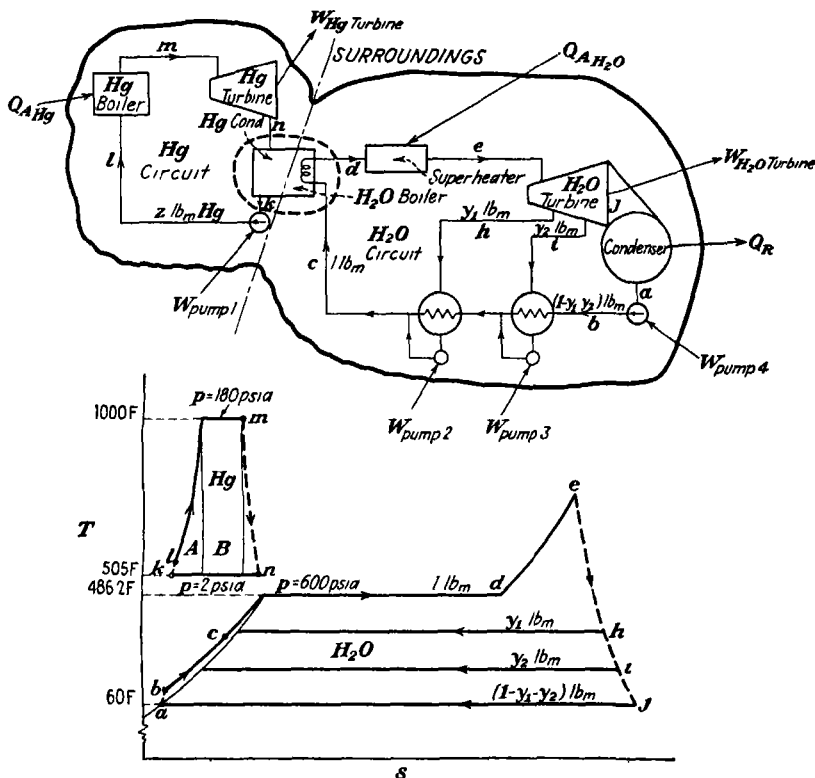


Fig 12-11 The binary-vapor system (temperature rise in pumps greatly exaggerated, complete detail not shown for H<sub>2</sub>O T-s diagram)

can be determined by an energy balance on the adiabatic system of Fig 12-12 (which is also shown in Fig 12-11)

$$\begin{aligned}
 Q - W &= \Delta h = 0 \\
 z(h_n - h_k) &= (h_d - h_c) \\
 z &= \frac{h_d - h_c}{h_n - h_k} \\
 z &= \frac{\text{Btu/lb}_m \text{ H}_2\text{O through boiler per period of time}}{\text{Btu/lb}_m \text{ Hg through boiler per period of time}} \\
 z &= \frac{\text{mass flow rate Hg}}{\text{mass flow rate H}_2\text{O}}
 \end{aligned}$$

The work and heat transfers for the binary-vapor system will be computed on the basis of 1 lb<sub>m</sub> flow of water through the boiler

$$Q_A = z(h_m - h_l) + (h_e - h_d) \frac{\text{Btu}}{\text{lb}_m \text{ H}_2\text{O through boiler}}$$

$$Q_R = (h_a - h_l)(1 - y_1 - y_2) \frac{\text{Btu}}{\text{lb}_m \text{ H}_2\text{O through boiler}}$$

$$W_{\text{turbines}} = z(h_m - h_n) + (h_e - h_k) + (h_h - h_i)(1 - y_1) \\ + (h_a - h_l)(1 - y_1 - y_2) \frac{\text{Btu}}{\text{lb}_m \text{ H}_2\text{O through boiler}}$$

The pump work is computed on the same basis noting that  $W_{p1}$  is for  $z$  lb<sub>m</sub> Hg;  $W_{p2}$  is for  $y_1$  lb<sub>m</sub> H<sub>2</sub>O,  $W_{p3}$  is for  $y_2$  lb<sub>m</sub> H<sub>2</sub>O,  $W_{p4}$  is for  $(1 - y_1 - y_2)$  lb<sub>m</sub> H<sub>2</sub>O

Thus, to achieve the objective of adding heat at the highest possible temperature, a binary-vapor cycle can be used since no one fluid is known that possesses all of the desirable characteristics of an ideal fluid. Mercury has certain advantages as a topping fluid (items 1, 2, 3, and 5, of Art 12-4). It also has disadvantages.

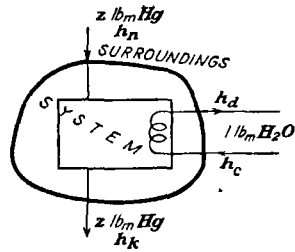


FIG 12-12 Flow system of mercury condenser and steam boiler

- 1 High cost The Kearny Station of the Public Service Electric and Gas Company of New Jersey produces 50,000 kw from a mercury-steam binary cycle. The binary system requires about 400,000 lb<sub>m</sub> Hg or approximately 8 lb<sub>m</sub> per net kilowatt output. Assuming a market value of \$1.00 lb<sub>m</sub> Hg, the mercury in the system represents an investment of \$400,000.
- 2 Not only are leaks from the system expensive, but also mercury vapor is quite toxic. Maintenance costs are increased to guard against leakage.
- 3 Mercury does not "wet" steel surfaces, and therefore heat transfer is hindered. The addition of small amounts of magnesium and titanium has largely eliminated this difficulty.
- 4 Iron is soluble in mercury at high temperatures, and therefore special steels must be used.

The mercury cycle at the Kearny Station operates between limits of 140 psig, 975 F, and 1 in. Hg pressure while developing 20,000 kw. The steam cycle operates between limits of 365 psig, 750 F, and 1 in. Hg pressure while developing 30,000 kw. The thermal efficiency of



the system is about 37 per cent. This efficiency has been exceeded only by the diesel engine, although the reciprocating engine is built in much smaller sizes (the largest engine in this country is about 8,000 hp) Moreover, internal-combustion engines require a more expensive fuel than external-combustion engines

Other fluids than mercury and water have been proposed for binary cycles: ammonia, methyl chloride, ethyl chloride, sodium dioxide, ethyl bromide, aluminum bromide, diphenyl, diphenyl oxide, although only the mercury-water cycle has a commercial history

**12-8. Other Performance Factors.** The *heat rate* is a logical factor for the cycle or for the complete station of furnace and cycle.

$$\text{Heat rate} = \frac{\text{heat transferred over a period of time}}{\text{work output during the same period of time}} \quad (12-4)$$

The *cycle heat rate* is defined as the heat received by the *cycle* per unit output of the *cycle*. The *station heat rate* is the ratio of the heating value of the fuel (the limiting amount of heat that can be transferred from the furnace) to the work output of the cycle. Both of these ratios usually include the efficiency of the electrical equipment.

A heat rate for the turbine cannot be logically justified because the turbine represents only one process in a cycle of processes. But it is quite usual to define a *turbine heat rate* which is based upon definitions and interpretations proposed by the ASME. Recourse must be made to this source for detailed methods when an official performance test on a steam turbine is to be made. The salient points, however, of the Code<sup>1</sup> are as follows.

**Complete Expansion Turbine** The turbine is charged with the enthalpy  $h_1$  of the steam supplied and credited with the enthalpy  $h_{f2}$  of the saturated liquid corresponding to the exhaust pressure. Then by Eq (12-4),

$$\text{Turbine heat rate} = \frac{h_1 - h_{f2}}{W} \left( \frac{\text{Btu}}{\text{kwhr}} \right) \quad (12-5)$$

Here

$$W = \frac{W_{\text{turbine}} (\text{Btu/lb}_m)}{3413 (\text{Btu/kwhr})} = \frac{\text{kwhr}}{\text{lb}_m}$$

**Reheating Turbine** The turbine is charged with the enthalpy  $h_1$  of the steam supplied plus the increase in enthalpy from reheating, and credited with the enthalpy  $h_{f2}$  of the saturated liquid correspond-

<sup>1</sup> "Power Test Codes, Steam Turbines," American Society of Mechanical Engineers, New York, 1941

ing to the exhaust pressure

$$\text{Turbine heat rate} = \frac{h_1 + \Delta h_{\text{reheat}} - h_{f2}}{W} \left( \frac{\text{Btu}}{\text{kwhr}} \right) \quad (12-6)$$

*Regenerative Turbine.* The turbine is charged with the enthalpy  $h_1$  of the steam supplied plus the enthalpy increase from pumps located *between* condenser and final heater and credited with the enthalpy  $h_8$  of the water leaving the final heater.

$$\text{Turbine heat rate} = \frac{m_1(h_1 - h_8) + \Sigma m(\Delta h)_{\text{pumps}}}{m_1 W} \left( \frac{\text{Btu}}{\text{kwhr}} \right) \quad (12-7)$$

and

$$m_1 = \text{mass flow rate to throttle of turbine}$$

Allowances are also made for makeup water, steam used for sealing glands, and subcooling of the condensate in the condenser

The *steam rate* is only applied to straight-expansion turbines, and it is the mass flow into the turbine per specified unit of output, pounds of steam per kilowatt-hour (or horsepower-hour) output

$$\text{Steam rate} = \frac{3413 \text{ (Btu/kwhr)}}{W_{\text{turbine}} \text{ (Btu/lb}_m\text{)}} = \left( \frac{\text{lb}_m \text{ steam}}{\text{kwhr}} \right) \quad (12-8a)$$

$$= \frac{2545 \text{ (Btu/hp-hr)}}{W_{\text{turbine}} \text{ (Btu/lb}_m\text{)}} = \left( \frac{\text{lb}_m \text{ steam}}{\text{hp-hr}} \right) \quad (12-8b)$$

In terms of the steam rate, the turbine heat rate equals,

$$\begin{aligned} \text{Turbine heat rate} &= (h_1 - h_{f2}) \frac{\text{Btu}}{\text{lb}_m} \left( \text{steam rate} \frac{\text{lb}_m}{\text{kwhr}} \right) = \frac{\text{Btu}}{\text{kwhr}} \\ &= (h_1 - h_{f2}) \left( \frac{3413}{W_{\text{turbine}}} \right) \end{aligned} \quad (12-9a)$$

And since the work ratio of the steam cycle is close to unity,

$$\text{Turbine heat rate} \approx \frac{3413}{\eta_i} = \text{cycle heat rate} \quad (12-9b)$$

**12-9. The Heat Reservoir and the Cycle.** It has been implied, in previous articles, that transfer of heat to the cycle was reversibly accomplished. This implication was adopted because the cycle was the center of attention and the presence of irreversibilities between cycle and heat reservoir would only confuse and not aid in the selection of the most efficient cycle. Now, however, let attention be directed to the heat reservoir. The heat reservoir is usually created by burning

a fuel with air at atmospheric pressure. This irreversible process produces a stream of hot gases at a temperature in the neighborhood of 3000 F, by passing the gases over the boiler, superheater, and economizer,<sup>1</sup> heat is transferred to a cycle. The gases of combustion should theoretically be cooled to the temperature of the atmosphere  $T_0$ , if the greatest amount of heat is to be transferred, although the attainment of this temperature is quite impossible as well as impractical (a temperature of 300 F is about the practical limit<sup>2</sup>). Suppose that the Carnot cycle of Example 1 is to be supplied with heat from this heat reservoir. Not only will the transfer of heat be irreversible, but the gases in the furnace could only be cooled to the highest temperature of the cycle, 946.2 R. If the Carnot cycle is replaced by the Rankine cycle of Example 3, the gases, theoretically, could be cooled essentially to atmospheric temperature because of the low-temperature heating process (*bc* in Fig. 12-3) in the Rankine cycle. Thus, the Rankine cycle is able to abstract a greater amount of heat from the practical heat reservoir than the Carnot is able to obtain. Substituting a Carnot cycle for a Rankine cycle will not necessarily improve the station heat rate unless other changes, still to be described, are also made. For the same reason, when the Rankine cycle is regenerated by using extraction heaters, the thermal efficiency of the cycle increases, but the efficiency<sup>2</sup> of the furnace decreases because the flue gases leave at higher temperatures than before. *The remedy is to find means for maintaining a constant efficiency of the furnace, no matter what changes are made in the cycle, for then the cycle of highest efficiency will also result in the highest over-all station efficiency.* The practical remedy is to install *air preheaters* near the exit of the furnace to cool the gases by transfer of energy to the air supplied for combustion of the fuel. In this manner, the efficiency of the furnace is held constant, while the temperature of combustion is raised and the transfer of heat is facilitated.

The type of firing limits the amount of air preheat. With stoker operation, the air temperature is limited to 300 or 400 F; else stoker maintenance problems arise; while pulverized fuel, oil, or gas allows higher air temperatures of 500 to 600 F. For a simple cycle such as the Rankine, air heaters are unnecessary, of course, because the flue-gas temperature can be held to a low and desirable value by the economizer.

<sup>1</sup> An economizer is a heat exchanger, placed near the exit of the furnace, wherein the cold feed water is heated by cooling the hot furnace gases.

<sup>2</sup> See Art. 11-14.

**12-10. The Availability Function and the Cycle.** It has been remarked that a cycle may have a low thermal efficiency and yet be operating in the most efficient manner. The thermal efficiency can be called a *First Law efficiency* because it shows only the energy ratio of the work delivered to the heat supplied to a cycle. A better gauge of efficiency is to measure the ratio of the work delivered to the available energy supplied to the cycle. Thus, a criterion of the performance of the cycle (quite independent of the thermal efficiency) can be called the *effectiveness*<sup>1</sup>  $\varepsilon$  and defined

$$\varepsilon = \left| \frac{\text{increase in available energy of the surroundings}}{\text{decrease in available energy of the surroundings}} \right| \quad (12-10)$$

For a power cycle the increase in available energy of the surroundings is equal to the work delivered by the cycle, and the decrease in available energy of the surroundings is equal to the *availability*<sup>2</sup> of the heat delivered by the surroundings

$$\varepsilon = \left| \frac{\Sigma W_{\text{cycle}}}{\alpha_{\text{surroundings}}} \right| \quad (12-11)$$

$\Sigma W$  = work delivered *by* cycle (a positive quantity)

$\alpha$  = availability of heat delivered *by* surroundings (a negative quantity)

Considering the fraction *within* the absolute-value sign of Eq (12-11), the algebraic sum of numerator and denominator represents available energy that the cycle has failed to convert into work. Therefore, the loss of available energy is

$$I = \alpha_{\text{surroundings}} + \Sigma W_{\text{cycle}} \quad (12-12)$$

$I$  = irreversibilities arising from temperature differences between system and surroundings, and also from irreversible processes within the system (a minus quantity)

**Example 7:** The Carnot cycle of Example 1 and the Rankine cycle of Example 3 are to use the heat reservoir of Example 5, Chap. V. Determine the effectiveness and the irreversibilities present.

**Solution:**

*Carnot cycle (B in Fig. D)*

The Carnot cycle can only cool the furnace gases from 3460 to 946.2 R, the heat irreversibly received by the cycle from each pound of furnace gas is

<sup>1</sup> Name adapted from Reference 2

<sup>2</sup> Refer to Art. 5-8

$$Q_A = \int_{946.2 \text{ R}}^{3460 \text{ R}} c_p dT = 0.25(3460 - 946.2) = 629 \text{ Btu/lb}_m \text{ gas}$$

(Note that, by convention, the heat leaving the reservoir is of minus sign, while the heat entering the system is of plus sign.) The work obtained from this quantity of heat is

$$\Sigma W = \eta_c Q_A = 0.45(629) = 282 \text{ Btu/lb}_m \text{ gas}$$

But the availability of the heat supplied by the surroundings was found in Example 5, Chap. V, to be  $-489 \text{ Btu/lb}_m^{-1}$  (The minus sign shows, by convention, a

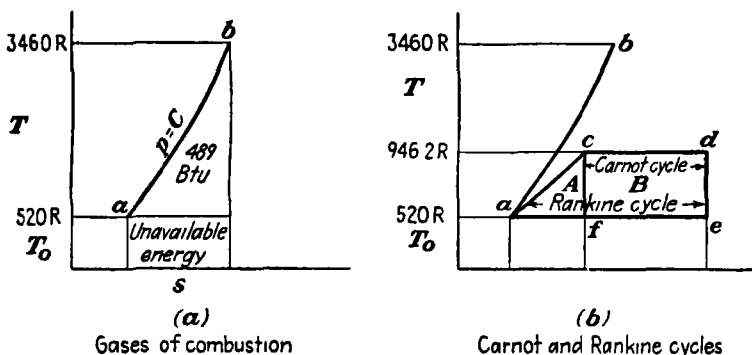


FIG. D

decrease in available energy of the surroundings.) Hence, the effectiveness of the cycle is

$$\varepsilon = \left| \frac{\Sigma W}{Q} \right| = \left| \frac{282}{-489} \right| = 0.58, \text{ or } 58 \text{ per cent} \quad \text{Ans}$$

The loss in available energy between heat reservoir and cycle because of temperature differences, and because the flue gases were not cooled to  $T_0$ , is

$$I = Q + \Sigma W = -489 + 282 = -207 \text{ Btu/lb}_m \quad \text{Ans}$$

Note that the cycle, itself, is internally reversible.

*Rankine cycle (A + B in Fig. D)*

The Rankine cycle can cool, at least theoretically, the furnace gases from 3460 R to essentially the surrounding temperature of 520 R. The heat received by the cycle from each pound of gas is

$$Q_A = \int_{520 \text{ R}}^{3460 \text{ R}} c_p dT = 0.25(3460 - 520) = 735 \text{ Btu/lb}_m \text{ gas}$$

The work obtained from this quantity of heat is

$$\Sigma W = \eta_c Q_A = 0.384(735) = 282 \text{ Btu/lb}_m \text{ gas}$$

The effectiveness and the irreversibilities, in this instance, are the same as for the Carnot cycle

$$\varepsilon = \left| \frac{\Sigma W}{Q} \right| = \left| \frac{282}{-489} \right| = 0.58, \text{ or } 58 \text{ per cent} \quad \text{Ans}$$

$$I = Q + \Sigma W = -489 + 282 = -207 \text{ Btu/lb}_m \text{ gas} \quad \text{Ans}$$

Thus, the station heat rate would be the same for either cycle. Although the Carnot cycle is a more efficient cycle than the Rankine, the Rankine cycle is able to abstract a greater amount of heat from the reservoir. (Note that the quantity of steam in one cycle differs from that in the other. Note, too, that the irreversibility of the combustion process is not included in the analysis.)

The availability of the heat supplied to the cycle is properly evaluated by examining the heat reservoir that is in the surroundings. However, the available energy of the real system is never increased by the same amount as the decrease in availability of the heat reservoir because temperature differences are always present (Example 7). The irreversibilities between heat reservoir and cycle, although important, may becloud the presence of irreversibilities within the cycle. For this reason the denominator of Eq. (12-11) will usually be evaluated by measuring the increase in available energy of the cycle from transfer of heat, and then assuming that this amount is equal (but of opposite sign) to the decrease in available energy of the surroundings. The increase in available energy can be found by treating the system as if it were a heat reservoir (Art. 5-8). In effect, it is assumed that the transfer of heat from reservoir to cycle is reversible, and therefore the irreversibilities all arise from irreversible processes *within* the system.

**Example 8:** Determine the effectiveness of the one-heater regenerative system of Example 6 and the irreversibilities within the system. (Atmospheric temperature is 60 F.)

**Solution:** The availability of the heat received by the cycle (and therefore the increase in available energy of the system from transfer of heat) is

$$Q_{\text{rev}}]_{p-c} = [\Delta h_{dh} - T_0 \Delta s_{dh}]_{\text{system}} \quad (5-8e)$$

From Example 6 and the Steam Tables,

600 psia, 740 F	$h_h = 1374.0$	$s_h = 1.6070$
600 psia, subcooled	$h_d = 243.7$	$s_d = 0.4000$
	$\Delta h = 1130.3$	$\Delta s = 1.2070$
$Q_{\text{rev}}]_{p-c} = 1130.3 - 519.7(1.2070) = 503.0 \text{ Btu/lb}_m$		

And therefore the decrease in available energy of the surroundings is assumed to be  $-503.0 \text{ Btu/lb}_m^{-1}$ . The work of the cycle was found in Example 6 to be

$$\Sigma W_{\text{irrev}} = 481.0 \text{ Btu/lb}_m$$

By Eqs (12-11) and (12-12)

$$\varepsilon = \frac{|\Sigma W|}{\alpha} = \frac{|481.0|}{|-503.0|} = 0.956, \text{ or } 95.6 \text{ per cent} \quad \text{Ans}$$

$$I = \alpha + \Sigma W$$

$$I = -503.0 + 481.0 = -22.0 \text{ Btu/lb}_m \text{ through boiler}$$

Since the only irreversible process in the cycle is the mixing process in the heater, then 22.0 Btu of available energy becomes, in the heater, unavailable energy for each pound of steam that flows through the boiler

**12-11. The Availability Function and the Process.** It will be of interest to examine the relationships that can be derived for the flow<sup>1</sup> process and to investigate means for evaluating the irreversibilities that may be present. Consider the general system in Fig 12-13, as

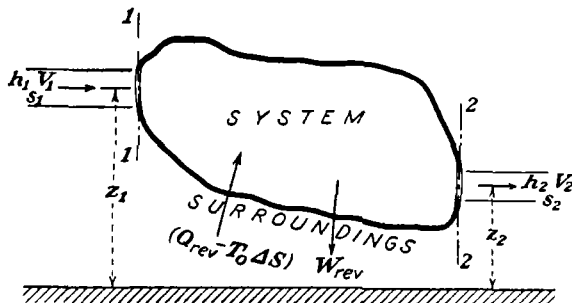


FIG 12-13 General flow system with reversible transfers of available energy

the fluid flows from state 1 to state 2, the available energy of the stream will change. The change in available energy of the system, the flow stream, can be evaluated by the method outlined in Art 5-8. Compute the available energy of all reversible heat and work transfers that are necessary to produce the desired end states for the process. Then, the change in available energy of the system will equal the change in available energy of the surroundings (but of opposite sign), because the process is reversible. Now if the system were to undergo the same change in state, except in an irreversible manner, the change in available energy for the fluid must be the same as before, but the transfer of available energy to (or from) the surroundings will be of lesser (or greater) amount than in the reversible case. Thus, if heat is reversibly added to the flow system of Fig 12-13, the available energy in the system will be increased by an amount equal to the availability of the heat

$$\begin{aligned} \text{Increase in available energy of system} &= Q_{\text{rev}} - T_0 \Delta s \\ &(\text{from reversible addition of heat to system}) \end{aligned}$$

<sup>1</sup> The same procedure, of course, can be used for nonflow processes (see Prob 35)

If work is reversibly done by the system, the decrease in available energy is

$$\begin{aligned} \text{Decrease in available energy of system} &= -W_{\text{rev}} \\ (\text{from reversible transfer of work to surroundings}) \end{aligned}$$

Adding these two terms gives the net change in available energy

$$\text{Change in available energy of system} = Q_{\text{rev}} - W_{\text{rev}} - T_0 \Delta s$$

But for any flow system,

$$Q - W = \Delta h + \Delta \text{KE} + \Delta \text{PE}$$

and therefore

$$\text{Change in available energy of system} = \Delta h - T_0 \Delta s + \Delta \text{KE} + \Delta \text{PE} \quad (12-13a)$$

A new property will be arbitrarily defined, it is called the *availability function*  $b$

$$b = h - T_0 s \quad \text{and} \quad \Delta b = \Delta h - T_0 \Delta s \quad (12-14)$$

And in terms of this function, for reversible or irreversible flow processes,

$$\text{Change in available energy of system} = \Delta b + \Delta \text{KE} + \Delta \text{PE} \quad (12-13b)$$

While, for the reversible process, the change in available energy of the system is reflected by a corresponding change in the available energy of the surroundings. Thus,

$$Q_{\text{rev}} - W_{\text{rev}} = \Delta b + \Delta \text{KE} + \Delta \text{PE} \quad (12-15)$$

Note that Eq (12-15) does not specify the *relative* amounts of work and availability that can be delivered to or from the surroundings while the state of the system is changing, because an infinite number of paths are possible and therefore an infinite number of combinations of work and availability are possible. This statement can be best illustrated by an example. In Fig 12-14, suppose that in a reversible flow process (without change in kinetic or potential energies) the state changes from 1 to 3 (the fluid is not necessarily steam). The change in available energy of the flow stream would be

$$\Delta b_{1-3} = \Delta h_{1-3} - T_0 \Delta s_{1-3}$$

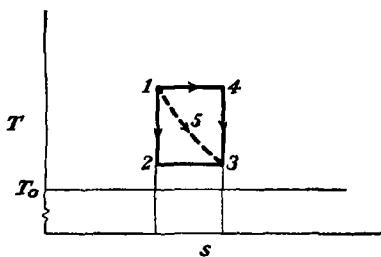


FIG 12-14 Different processes for the same change in state



By path 1-2-3, the change in available energy is

$$\begin{aligned}
 1-2 \text{ Decrease in available energy} &= h_2 - h_1 \\
 &\quad (\text{from transfer of work}) \\
 2-3 \text{ Increase in available energy} &= Q_{\text{rev}} - T_0(s_3 - s_2) \\
 &\quad (\text{from transfer of heat}) \\
 2-3 \text{ Decrease in available energy} &= (h_3 - h_2) - Q_{\text{rev}} \\
 &\quad (\text{from transfer of work}) \\
 \text{Net change in available energy} &= (h_3 - h_1) - T_0(s_3 - s_1) \\
 &= \Delta b_{1-3}
 \end{aligned}$$

Or by path 1-4-3, the change in available energy is

$$\begin{aligned}
 1-4 \text{ Increase in available energy} &= Q_{\text{rev}} - T_0(s_4 - s_1) \\
 &\quad (\text{from transfer of heat}) \\
 1-4 \text{ Decrease in available energy} &= (h_4 - h_1) - Q_{\text{rev}} \\
 &\quad (\text{from transfer of work}) \\
 4-3 \text{ Decrease in available energy} &= h_3 - h_4 \\
 &\quad (\text{from transfer of work}) \\
 \text{Net change in available energy} &= (h_3 - h_1) - T_0(s_3 - s_1) \\
 &= \Delta b_{1-3}
 \end{aligned}$$

Thus, the change in the availability function between states 1 and 3 shows the *net* change in available energy of the system (the flow stream), but it does not show the relative transfers of work and availability, for these quantities depend on the reversible path selected for the process. When the process is reversibly conducted, the net change in available energy of the system will be compensated by a corresponding change in available energy of the surroundings.

Suppose the actual process is irreversible and adiabatic along path 1-5-3. This path cannot be followed by a reversible and adiabatic process, but it can be followed by a reversible process if heat is added to the system

$$\begin{aligned}
 1-5-3 \text{ Decrease in available energy} &= \Delta h - Q_{\text{rev}} = h_3 - h_1 - \int_1^3 T ds \\
 &\quad (\text{from transfer of work to} \\
 &\quad \text{surroundings}) \\
 1-5-3 \text{ Increase in available energy} &= Q_{\text{rev}} - T_0 \Delta s = \int_1^3 T ds - T_0(s_3 - s_1) \\
 &\quad (\text{from transfer of heat to} \\
 &\quad \text{system}) \\
 \text{Net change in available energy} &= \Delta h - T_0 \Delta s = (h_3 - h_1) - T_0(s_3 - s_1) \\
 &= \Delta b_{1-3}
 \end{aligned}$$

Thus, if the process were reversible, the available energy transferred between system and surroundings in the forms of both work and heat would be, as before,  $\Delta b$ . Since the real process is irreversible and adiabatic, only work is supplied to the surroundings of amount  $-\Delta h$ . The loss of available energy, of course, is the algebraic sum of the changes in available energy for both system and surroundings  $\Delta b_{1-3} + W_{1-3}$ .

A Second Law efficiency of the process can be proposed in the same manner as for a cycle. The *effectiveness of the process* can be defined

$$\varepsilon = \left| \frac{\text{increase in available energy}}{\text{decrease in available energy}} \right| \quad (12-16)$$

Here the locations of the increase and decrease in available energies are not specified for reasons that will be apparent in the following examples. The algebraic sum of the numerator and the denominator of the fraction within the absolute value sign of Eq. (12-16) represents, as before, the loss in available energy because of irreversibilities in the process, and this difference equals

$$I = \Sigma \text{ changes in available energy} = -T_0 \Sigma \Delta S \quad (12-17)$$

*The Effectiveness of the Turbine* Consider the adiabatic but irreversible process for a steam turbine illustrated in Fig. 12-15. Saturated steam enters the turbine at state 1 and leaves at state 3, the entropy increases in this process because of the

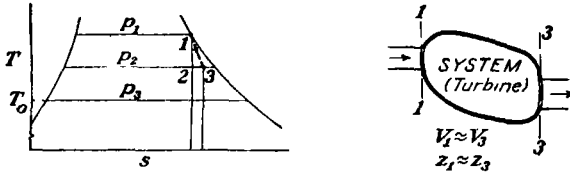


FIG. 12-15 Steam turbine with irreversible adiabatic expansion

irreversibilities (Art. 5-10). The work done by the system is found by the First Law equation

$$\begin{aligned} Q - W &= \Delta h \quad \text{and} \quad Q \approx 0 \\ -W &= h_3 - h_1 \end{aligned}$$

The decrease in available energy for the flow stream (the system) is found by the Second Law equation

$$\begin{aligned} \Delta b &= \Delta h - T_0 \Delta s \\ &= (h_3 - h_1) - T_0(s_3 - s_1) \end{aligned} \quad (12-14)$$

The only effects of this process are an increase in the available energy of the surroundings ( $+W$ ) and a decrease in the available energy of the system ( $\Delta b$ ). Therefore, the effectiveness is equal to

$$\varepsilon = \left| \frac{\text{increase in available energy (of surroundings)}}{\text{decrease in available energy (of system)}} \right| \quad (12-16)$$

$$\varepsilon = \left| \frac{W}{\Delta b} \right| \quad (12-16a)$$

$$\varepsilon = \left| \frac{h_1 - h_3}{h_3 - h_1 - T_0(s_3 - s_1)} \right|$$

The loss of available energy is equal to the algebraic sum of the numerator and denominator of the fraction within the bars.

$$I = \Delta b + W = \Delta b - \Delta h = -T_0 \Delta s \quad (12-17a)$$

The engine efficiency is a more usual gauge of the performance of the turbine

$$\eta_e = \frac{W_{\text{actual}}}{W_{\text{isen}}} \quad (12-2)$$

Since the real turbine undergoes, essentially, an adiabatic process,

$$\eta_e = \frac{h_1 - h_3}{h_1 - h_2}$$

Here the difference between numerator and denominator represents, directly, work that was not obtained because the process was irreversible. To the practical man this difference is a loss in available energy, but to the theorist it is not an entire loss. For the fluid leaving the system of Fig. 12-15 could be cooled from state 3 to state 2, and the availability of the heat obtained from this cooling process would be

$$Q_{\text{rev}}]_{p-c} = \Delta h - T_0 \Delta s = h_2 - h_3 - T_0(s_2 - s_3)$$

Then, if this heat were transferred to a reversible cycle, work could be done while the fluid was being restored to the state that would have been attained by a reversible expansion, state 2. The entire work would be

$$\begin{aligned} -W_{1-3} &= h_3 - h_1 \\ -W_{3-2}]_{\text{rev}} &= h_2 - h_3 - T_0(s_2 - s_3) \\ \Sigma W_{1-2} &= h_1 - h_2 - T_0(s_3 - s_2) \end{aligned}$$

which is less than the isentropic work  $(h_1 - h_2)$  by the amount

$$-T_0 \Delta s_{2-3} = -T_0 \Delta s_{1-3}$$

and this amount is the loss in available energy predicted by the availability function. Thus, it is again demonstrated that  $-T_0 \Sigma \Delta s$  is the entire loss in available energy for the irreversible process. However, and it must be emphasized, the usual turbine system cannot be readily adapted to serve as a heat reservoir for a hypothetical and reversible cycle, for this reason the engine efficiency is the preferred gauge of turbine performance.

The effectiveness of the turbine has a larger value than the engine efficiency because the system is credited with its potentialities to serve as a heat reservoir for a hypothetical engine. As the terminal state of the fluid approaches  $T_0$  (Fig. 12-15, as  $p_2$  approaches  $p_s$ ), the availability of any potential transfer of heat is decreased and the effectiveness and engine efficiency approach the same value.

**Example 9:** Superheated steam at 400 psia and 600 F enters a turbine and emerges at a pressure of 50 psia and quality of 99.5 per cent. Compute the engine efficiency, effectiveness, and the loss of available energy for the process. (Atmospheric temperature is 60 F.)

**Solution:** From the Steam Tables

$$p_1 = 400 \text{ psia} \quad t_1 = 600 \text{ F} \quad h_1 = 1306.9 \quad s_1 = 1.5894 \quad b_1 = 480.9$$

With isentropic expansion to 50 psia (Mollier chart)

$$p_2 = 50 \text{ psia} \quad x = 0.945 \quad h_{2 \text{ isen}} = 1122 \quad s_2 = 1.5894$$

At the end state for the irreversible expansion

$$p_2 = 50 \text{ psia} \quad x = 0.995 \quad h_1 = 1169.5 \quad s_1 = 1.6522 \quad b_1 = 310.9$$

With these values,

$$\begin{aligned} -W &= \Delta h = h_2 - h_1 = 1169.5 - 1306.9 & W &= 137.4 \text{ Btu/lb}_m \\ \Delta b &= b_2 - b_1 = 310.9 - 480.9 = -170.0 \text{ Btu/lb}_m \\ \Delta h_{isen} &= 1306.9 - 1122 = 184.9 \text{ Btu/lb}_m \\ \eta_s &= \frac{W}{-\Delta h_{isen}} \end{aligned} \quad (12-2)$$

$$\eta_s = \frac{137.4}{184.9} = 0.745, \text{ or } 74.5 \text{ per cent} \quad \text{Ans}$$

$$\varepsilon = \left| \frac{W}{\Delta b} \right| \quad (12-16a)$$

$$\varepsilon = \left| \frac{137.4}{-170.0} \right| = 0.81, \text{ or } 81 \text{ per cent} \quad \text{Ans.}$$

$$I = \Delta b + W \quad (12-17a)$$

$$I = -170.0 + 137.4 = -32.6 \text{ Btu/lb}_m \quad \text{Ans}$$

*The Effectiveness of the Pump* The pump (or compressor) process is but the inverse process to that of a turbine. Here work is supplied by the surroundings of amount

$$\begin{aligned} Q - W &= \Delta h \\ W &= -\Delta h \end{aligned} \quad Q \approx 0$$

The flow stream (the system) in this instance experiences an increase in available energy, of amount,

$$\Delta b = \Delta h - T_0 \Delta s$$

Since these are the only effects of the process, the effectiveness of the pump can be defined

$$\varepsilon = \left| \frac{\text{increase in available energy (of system)}}{\text{decrease in available energy (of surroundings)}} \right| \quad (12-16)$$

$$\varepsilon = \left| \frac{\Delta b}{W} \right| = \left| \frac{\Delta b}{-\Delta h} \right| \quad (12-16b)$$

The loss of available energy is found, as before, to be the algebraic sum of the numerator and denominator of the fraction within the bars

$$I = \Delta b + W = \Delta b - \Delta h = -T_0 \Delta s \quad (12-17b)$$

When a liquid is pumped, the small change in entropy is difficult to evaluate accurately, for this reason the accuracy of the over-all computation becomes somewhat doubtful

**Example 10** Compute the effectiveness and irreversibilities present in the compression process of Example 2

**Solution:** Examples 1 and 2 contain the following data

$$\begin{aligned} h_a &= 348.5 & s_a &= 0.6720 \\ h_b &= 471.6 & s_b &= 0.6720 \\ h_{b'} &= 492.7 & s_{b'} &= 0.6944 \\ \eta_c &= 85 \text{ per cent} \end{aligned}$$

The effectiveness equals

$$\begin{aligned}\varepsilon &= \left| \frac{\Delta b}{-\Delta h} \right| = \frac{(h_b - h_a) - T_0(s_b - s_a)}{-(h_b - h_a)} \\ &= \left| \frac{144.2 - 11.6}{-144.2} \right| = 0.92, \text{ or } 92 \text{ per cent} \quad \text{Ans.}\end{aligned}$$

The loss of available energy is

$$\begin{aligned}I &= \Delta b - \Delta h \\ I &= -11.6 \text{ Btu/lb}_m \quad \text{Ans.}\end{aligned}$$

*The Effectiveness of the Heater* Consider the open heater of Fig 12-9a, in the irreversible process  $y$  lb<sub>m</sub> of fluid, in passing from state  $i$  to state  $c$ , is decreased in available energy by the amount

$$y(b_c - b_i)$$

while  $(1 - y)$  lb<sub>m</sub> of fluid, in passing from state  $b$  to state  $c$ , is increased in available energy by the amount

$$(1 - y)(b_c - b_b)$$

The effectiveness of the heat exchanger can be defined

$$\varepsilon = \frac{\left| \begin{array}{l} \text{increase in available energy (of a flow path)} \\ \text{decrease in available energy (of a flow path)} \end{array} \right|}{\quad} \quad (12-16)$$

$$= \left| \frac{(1 - y)(b_c - b_b)}{y(b_c - b_i)} \right| \quad (12-16c)$$

The irreversibility of this mixing process is

$$I = y(b_c - b_i) + (1 - y)(b_c - b_b) \quad (12-17c)$$

$$I = \Sigma m \Delta b = -T_0 \Sigma \Delta S \quad (12-17d)$$

The same procedure can be followed for the closed heater of Fig 12-9b. Either the entire system of heater, pump, and mixing point can be analyzed as one unit, or else each component can be separately analyzed. Thus, the effectiveness of the heater alone in Fig 12-9b is shown by Eq (12-16) to be

$$\varepsilon = \left| \frac{(1 - y)(b_i - b_b)}{y(b_i - b_i)} \right|$$

or the effectiveness of the entire system of Fig 12-9b can be considered to be

$$\varepsilon = \left| \frac{(1 - y)(b_c - b_b)}{[y(b_c - b_i) + W_p]} \right| = \left| \frac{(1 - y)(b_c - b_b)}{y[(b_c - b_i) + (h_i - h_k)]} \right| \quad (12-16d)$$

Note that the mixing point is equivalent to a system like that in Fig 12-9a

**Example 11:** Determine the effectiveness and the loss of available energy in the heater of Example 6, and compare with the answer to Example 8 (Atmospheric temperature is 60 F)

**Solution:** The data are obtained from Example 6:<sup>1</sup>

$$\begin{array}{lll} y = 0.195 & 1 - y = 0.805 & \\ h_b = 28.19 & s_b = 0.0555 & b_b = -0.65 \\ h_c = 241.95 & s_c = 0.4000 & b_c = 34.07 \\ h_1 = 1126 & s_1 = 1.6070 & b_1 = 290.85 \end{array}$$

With these values, the effectiveness is found by Eq. (12-16c) to be

$$\epsilon = \left| \frac{(1-y)(b_c - b_b)}{y(b_c - b_1)} \right| = \left| \frac{0.805(33.95 + 0.67)}{0.195(33.95 - 290.4)} \right| = \left| \frac{28.0}{-50.0} \right| \\ = 0.56, \text{ or } 56 \text{ per cent} \quad \text{Ans}$$

The loss in available energy is

$$I = -50.0 + 28.0 = -22.0 \text{ Btu/lb}_m \quad \text{Ans}$$

(which agrees with the answer found in Example 8)

*The Condenser* Although the condenser is essentially a closed heater, such as that illustrated in Fig. 12-9b, its function is not to heat the circulating water but, rather, to maintain the lowest possible temperature for the condensation of the fluid in the cycle. Since the coolant for the condenser can not be used for any useful purpose, the increase in available energy of the cooling water can be considered to be zero (and, practically, the increase approaches zero because of the high rate of flow of cooling water through the condenser). Thus, the decrease in available energy of the steam in passing through the condenser is not partially compensated by an increase in available energy of the surroundings, and therefore the loss of available energy debited to the condenser can be considered to be

$$I = \Sigma m \Delta b = m \Delta b_{\text{cycle fluid}} \quad (12-17e)$$

(because  $\Delta b$  for the condenser cooling water is zero)

The loss of available energy in the condensation process arises, of course, because of the temperature difference between coolant water ( $T_0$ ) and steam ( $T_R$ ).

*The Reheater* A steam reheater may be located in the furnace to reheat the steam before its final expansion takes place in the low-pressure turbine. The effectiveness of the reheater could be defined in terms of the decrease in available energy of the gases in the furnace and the increase in available energy of the fluid in the reheater. But, in most instances, the change in state of the combustion gases is unknown, and the increase in available energy of the fluid in the reheater from addition of heat is the object of interest. Unfortunately, this particular increase in available energy cannot be exactly found when the reheater contains a frictional process. For example, steam may enter the reheater at a pressure of 50 psi and emerge at a lower pressure of 40 psi. Although the net change in available energy is evaluated by  $\Delta b$ , this evaluation is not equal to the increase in available energy from transfer of heat. Rather, the change in  $\Delta b$  is equal to the decrease in  $\Delta b$  in the throttling operation, a loss in available energy, plus the increase in  $\Delta b$  from addition of heat. Either this discrepancy can be ignored or the following expedient can be arbitrarily adopted. The reheater can be considered

<sup>1</sup> Since the Steam Tables are based upon an arbitrary datum, the value of the function  $b$  can have positive or negative values.

to contain two processes, a throttling process, followed by a constant-pressure heating process. The increase in available energy from transfer of heat is found only for the latter process while the loss of available energy in the throttling process is debited against the cycle.

**12-12. Second Law Analysis of the Power Plant.** A Second Law analysis of a power system can be made by evaluating the changes in available energy and the irreversibilities that occur in each process. A logical method of analysis would be to determine the following quantities:

1. The decrease in available energy of the furnace, and, therefore, the availability of the heat supplied to the cycle (Example 5, Chap V)
2. The increase in available energy of the system from transfer of heat (Eq 5-8d)
3. The loss of available energy between heat reservoir and system (Example 7)
4. The loss of available energy for each element of the system
  - a. The turbine [Eq (12-17a)]
  - b. The pump(s) [Eq (12-17b)]
  - c. The heater(s) [Eq (12-17c) and, for heater, pump, and mixing point, algebraic sum of the numerator and denominator of Eq (12-16d)]
  - d. The condenser [Eq (12-17e)]
5. The net work done by the power system

The difference between (1) and (5) is the total of the irreversibilities (losses of available energy) that are present in the system of cycle and heat reservoir (but not including the combustion process). When the furnace is excluded from the analysis, the difference between (2) and (5) is the total of the irreversibilities in the cycle alone.

**12-13. The Availability of the System.** The availability of heat has been defined as the maximum work that can be obtained from transformation of heat into work by a reversible cycle (Art 5-8). Thus, the term has designated the part of a heat transfer that can be called *available energy*. This is a restricted definition that was adopted to clarify the steps in the analyses of problems. Most generally, availability is used as a synonym, not only for the available part of heat, but also for the total available energy of the system. Since a means can always be found for converting available energy into work, a broader definition of availability can be proposed

**Availability is the maximum work that can be produced from the available energy of the system.**

In this transformation, the earth or its atmosphere<sup>1</sup> may serve as a heat reservoir for the system

In evaluating the availability of heat, the temperature of the atmosphere is the barrier that divides the energy in the system into two parts, available and unavailable energies. Heat can be abstracted from a reservoir only to the stage where the temperature of the reservoir becomes equal to the temperature of the atmosphere. In similar manner, the pressure of the atmosphere is the practical limiting barrier to the transformation of energy into work by expansion of the system.<sup>2</sup> Then, the available energy of the system is measured by the amount of available energy that can be reversibly transferred to the surroundings while the state of the system is reduced to a dead state. The dead state is defined as one where all potentials of the system that could cause a change are in balance with those of the surroundings. Since the earth and its atmosphere are the ultimate surroundings (Art 4-1), the temperature and pressure of the atmosphere are the limiting factors for evaluating the available energy of the system.<sup>3</sup> Of course, if kinetic and potential energies are present, these forms of available energy can be independently evaluated

The availability of a fluid in steady flow (the maximum work that can be obtained either directly or indirectly from the energy in the fluid) can be found from

$$\mathcal{Q}_{\text{rev}} - W_{\text{rev}} = \Delta b + \Delta \text{KE} + \Delta \text{PE} \quad (12-15)$$

by specifying that the final state of the fluid is to be a phase that can exist in equilibrium with the atmosphere

$$p_{\text{final}} = p_0 \quad T_{\text{final}} = T_0 \quad b_{\text{final}} = b_0 \quad V_{\text{final}} = 0 \quad z_{\text{final}} = 0$$

$$(-)\text{Availability} = \mathcal{Q}_{\text{rev}} - W_{\text{rev}} = b_0 - \left( b_1 + \frac{V_1^2}{2g_c J} + \frac{g}{g_c} z_1 \right) \quad (12-18a)$$

<sup>1</sup> The term *atmosphere* implies the rivers and lakes as well as the air of the earth

<sup>2</sup> Unless a lower pressure than atmospheric can be confined *within* the system (footnote, p 415), even then, a pump will be required to force the fluid to leave the system against the resistance of the atmosphere

<sup>3</sup> This assumes that the fluid leaving the system is stable and inert in the presence of the atmosphere (although chemical reactions may be present within the system).



(The negative sign is a necessary convention because availability is considered to be a positive quantity when work can be done by the system) If all transfers of heat are restricted to the temperature  $T_0$ , the maximum work can be obtained without resorting to a reversible engine for the conversion of heat into work.

$$\text{Availability} = W_{\text{rev}}]_{Q \text{ at } T_0} = \left( b_1 + \frac{V_1^2}{2g_c} + \frac{g}{g_c} z_1 \right) - b_0 \quad (12-18b)$$

The availability and, also, Eqs (12-18a) and (12-18b) can be visualized by means of Fig 12-16. Here the problem is to evaluate the availability of saturated steam in steady flow at a pressure of 1000 psia when the atmospheric pressure is 14.7 psia and atmospheric temperature is 60 F. The fluid leaving the system is to be in equilibrium with the atmosphere, therefore, the phase at exit (state 5)

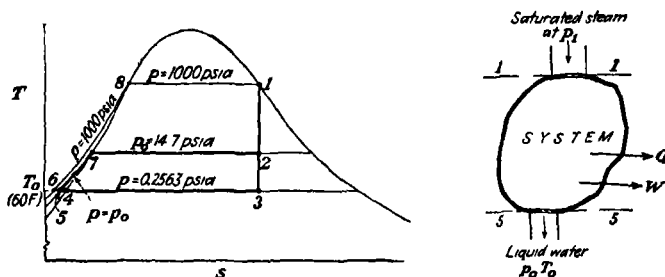


FIG 12-16 The availability of a flowstream (surroundings at  $t_0 = 60^\circ\text{F}$ ,  $p_0 = 14.7$  psia)

must be liquid (since  $\text{H}_2\text{O}$  cannot exist as steam at atmospheric pressure and temperature). Then, either Eq (12-18a) or (12-18b) can be solved with values for states 1 and 5 for saturated steam and subcooled water, respectively, selected from the Steam Tables<sup>1</sup>. The net work, evaluated by Eq (12-18b), can be obtained from this system in the following processes. Isentropic expansion from state 1 to 3, condensation from state 3 to state 4, isothermal compression from state 4 (pressure less than atmospheric) to state 5 (pressure atmospheric). Note that the *availability* of the fluid at states between 4 and 3 at  $T_0$  is a negative quantity (whether or not the function  $b$  is positive or negative), since the pressure is less than atmospheric. Because of this negative availability, work must be supplied to the system (process 4-5) to restore the fluid to the dead-state pressure  $p_0$ . If another path than 1-3-4-5 is selected, the work done by the system will be changed in value, but the net sum of the work and the available part of the heat transfer will be constant and equal to the availability of the steam in its initial state. Thus, work could be obtained by expanding from state 1 to 2 (atmospheric pressure), and then heat could be transferred to a reversible cycle while the system was cooled from state 2 to 7 to state 5. The work done by the system plus the work done by the reversible cycle will equal, as before, the initial availability of the steam (Eq 12-18a).

<sup>1</sup> The algebraic sign of the availability function  $b$  will be affected, of course, by the datum state arbitrarily selected by the maker of the Steam Tables

It is also possible for the fluid to be at a temperature less than  $T_0$  although the available energy (the availability) is not zero. Consider Fig 12-17. The temperature of the fluid at state 3 is less than  $T_0$ , and the pressure is  $p_0$ , but the availability is greater than zero. That this statement is true can be shown by borrowing work from the surroundings to compress isentropically the fluid from state 3 to 1. The fluid at state 1 can be isothermally expanded to the dead state 2, and the work obtained from this process can be used, in part, to repay the loan of work that was required for process 3-1. The work remaining is equal in amount to the availability of the fluid in state 3. (Note that the heat transferred from the surroundings in process 1-2 did not decrease the available energy<sup>1</sup> of the surroundings because the transfer occurred at a temperature of  $T_0$ .)

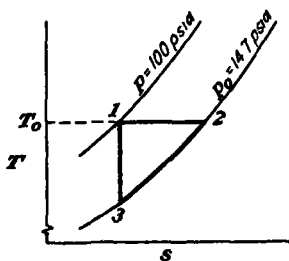


FIG 12-17 Availability of a system at a temperature less than  $T_0$

### Problems

The following items may also be specified by the teacher in the solution of the problems

- |  |   |
|--|---|
| a Thermal efficiency                         | j $h$ s diagram   |
| b Heat added                                 | k Heat rate for cycle (kw-hr)                             |
| c Heat rejected                              | l Heat rate for cycle (hp-hr)                             |
| d Turbine work                               | m Station heat rate (kw-hr)                               |
| e Pump work                                  | (Assume 10,000 Btu lb <sub>m</sub> <sup>-1</sup> coal and |
| f Work ratio                                 | furnace efficiency of 85 per cent)                        |
| g Error arising by neglecting pump work      | n Steam rate (kw-hr)                                      |
| h $T$ s diagram to illustrate heat transfers | o Steam rate (hp-hr)                                      |
| i $p$ v diagram                              | p Mollier chart not permitted for solution                |
|  | q Neglect pump work                                       |

Unless other information is given in the problem, the temperature ( $T_0$ ) and pressure ( $p_0$ ) of the atmosphere can be assumed to be 60 F and 14.7 psia.

1. Determine the thermal efficiency, the work of each process, and the work ratio for a Carnot cycle that uses steam as the working fluid in a series of flow processes. The condition of the steam at the start of the isothermal addition of heat is 600 psia and 90 per cent moisture, at the end of the heating process the state of the steam is 600 psia and 5 per cent moisture. The heat-rejection process is at a pressure of 1 in. Hg. Repeat the problem, assuming that each process is nonflow with the fluid being confined in a cylinder by a piston.

2. Assume that upon test of the cycle of Prob. 1 the compression and expansion efficiencies are each found to be 75 per cent, and both processes are adiabatic. Compute the thermal efficiency and the work ratio.

3. A Rankine cycle is supplied with saturated steam at 400 psia, and the pressure in the condenser is 1 in. Hg. Determine the thermal efficiency, work of

<sup>1</sup> Of course, the positive availability of the fluid in state 3 arises from the work that was added in some earlier process to refrigerate the fluid.

each flow process, heat rejected, and the work ratio Repeat the problem, assuming that the processes are all nonflow

4. Assume that, upon test of the cycle of Prob 3, the compression and expansion efficiencies are each found to be 75 per cent, and both processes are adiabatic Compute the thermal efficiency and the work ratio

5. A Rankine cycle is supplied with superheated steam at 400 psia and 700 F, and the pressure in the condenser is 1 in Hg Determine the thermal efficiency, heat rejected, and the work ratio

6. Upon test of the cycle of Prob 5, the compression and expansion efficiencies are found to be 75 per cent, and both processes are adiabatic Compute the thermal efficiency and the work ratio

7. Repeat Prob 6, using the method of analysis demonstrated in Art 12-3

8 The nozzles in the turbine of Prob 5 pass 20,000 lb<sub>m</sub> hr<sup>-1</sup> of steam Compute the horsepower of the turbine and the quantity of cooling water demanded by the condenser if the temperature rise of the coolant is 10 F

9 Upon test of the cycle in Prob 5, the turbine steam rate is found to be 9.5 lb<sub>m</sub> kw hr<sup>-1</sup> Determine, for the actual cycle, the thermal efficiency and the engine efficiency, if the compression efficiency is 60 per cent (The work processes are adiabatic)

10 The Rankine cycle of Prob 5 is converted into a reheat cycle The steam is reheated at constant pressure from an initial state of 10 per cent moisture to 700 F Determine the thermal efficiency and the heat rejected for the cycle

11 Repeat Prob 10 but for the data of Prob 6

12. Steam at 1,200 psia and 800 F enters a high-pressure turbine and adiabatically expands with engine efficiency of 85 per cent to a state of 5 per cent moisture The steam is then reheated to 600 F but with pressure drop of 10 psia before it enters the low-pressure turbine where the engine efficiency is 82 per cent for the adiabatic expansion Determine the thermal efficiency of the cycle if the compression efficiency of the adiabatic water pump is 60 per cent and the condenser vacuum is 28.93 in Hg

13 The cycle of Prob 6 is governed by throttling, and at part load the steam enters the turbine nozzles at a pressure of 300 psia Compute the thermal efficiency, and draw the *Ts* diagram for this cycle

14 Repeat Prob 9, assuming that the steam rate includes a generator efficiency of 85 per cent

15. A regenerative cycle operates between limits of 1200 psia, 1000 F, and 1 in Hg Compute the thermal efficiency if one heater is used, of the type shown in Fig 12-9a, at the optimum extraction pressure Engine efficiency of turbine and compression efficiency of pumps are each 100 per cent

16. For the data of Prob 15 vary the extraction pressure between limits of 1 in Hg and 1,200 psia, and construct a curve showing the relationship between thermal efficiency and extraction pressure

17. Repeat Prob 15 for two heaters

18. Repeat Prob 15 for three heaters

19. Repeat Prob 15, assuming that the engine efficiency is 85 per cent up to the extraction point and 82 per cent for the entire expansion (Pump efficiency is unchanged)

20. Repeat Prob 15, assuming that the engine efficiency of the regenerative turbine is 82 per cent

**21.** Repeat Prob 15, but also assume the steam is reheated to the initial temperature at the extraction pressure (Extracted steam is not to be reheated)

**22.** A reheat-regenerative cycle has two extraction heaters similar to Fig 12-9b. For the real system terminal differences and throttling exist. Draw a  $Ts$  diagram showing throttling and temperature drop from superheater to high-pressure turbine, irreversible expansion in high-pressure turbine, pressure drop in reheater, pressure and temperature drop from reheater to low-pressure turbine, and irreversible expansion in low-pressure turbine. All pumps are irreversible. Label reasons (causes) on the diagram for all irreversibilities.

**23.** Top the regenerative cycle of Example 6 with a reversible mercury cycle that operates between limits of 180 psia (saturated) and 2 psia. Compute the thermal efficiency for the binary cycle and for each cycle considered alone.

**24.** Top the Rankine cycle of Prob 6 with a mercury cycle that operates between limits of 180 psia (saturated) and 1 psia. The compression and engine efficiencies are 75 per cent in both cycles, and all work processes are adiabatic. Compute the thermal efficiencies for the binary cycle and for each cycle considered alone.

**25.** Repeat Prob 23 but for the data of Example 3, and compare the answer to that of Prob 23. Explain thoroughly all aspects of this problem that are revealed by the answers.

**26.** Determine the effectiveness of the cycle in Prob 4 based upon the availability of the heat leaving the heat reservoir (Use data of Example 5, Chap. V). Locate the irreversibilities.

In following problems the heat reservoir will be ignored and only internal irreversibilities of the cycle will be considered.

**27.** Determine the effectiveness of the cycle in Prob 4 and the nature and total amount of irreversibilities.

**28.** Determine the effectiveness of the cycle and of each turbine in Prob 12, and evaluate each irreversibility in the cycle.

**29.** Determine the effectiveness of cycle and turbine in Prob. 13, and evaluate each irreversibility in the cycle.

**30.** Compute the effectiveness of the cycle, and of the turbines and heater, for the data of Prob 19, and evaluate each irreversibility in the cycle.

**31.** Compute the effectiveness of the binary cycle, and of the turbines and heater, for the data of Prob 24, and evaluate each irreversibility in the system.

**32.** A Rankine cycle is supplied with saturated steam at 400 psia while the condenser temperature is 60 F. It is proposed to convert this cycle into a regenerative cycle. The cycle is to have one open heater with the extraction point at the initial state of the steam, 400 psia (saturated). Heat is added only to vaporize the saturated water entering the boiler at constant temperature and pressure. Calculate the thermal efficiency and effectiveness for the cycle before and after the change, and the irreversibility of the mixing. What was gained and what was lost in the conversion if it is assumed that different heat reservoirs can be found for each cycle so that transfer of heat is reversible?

**33.** A Rankine cycle is to be performed by 1 lb<sub>m</sub> H<sub>2</sub>O confined in a cylinder by a piston. The limits of the cycle are 400 psia (saturated) to 1 psia. Determine the volume change and heat added for each process in the cycle.

**34.** Determine the availability of 1 lb<sub>m</sub> air in steady flow at states 1, 2, and 3 of Fig 12-17 if the temperature at state 3 is 400 R. (Assume that changes in kinetic and potential energies are negligible.)

**35.** Derive an equation for the availability of a nonflow system. (Follow the same procedure as in Art. 12-11 except that

$$Q - W = \Delta u$$

and the net work (the availability) transferred to the surroundings differs from the gross work by the amount  $p_0 \Delta v$ .) Note that the decrease in available energy from transfer of work equals

$$-W_{\text{rev}} + p_0 \Delta v$$

**36.** A simple steam cycle operates between 400 psia and 600 F to 1 in Hg with engine efficiency of the turbine of 0.80. Compute the effectiveness of the cycle if the boiler feed pump is reversible. (The ideal cycle for this system is the Rankine cycle.)

**37.** Compute the amount of irreversibility for the condenser of Prob 36.

**38.** A turbine receives steam at 400 psia and 600 F and exhausts at 50 psia. The irreversibility for this adiabatic process is 34 Btu lb<sub>m</sub><sup>-1</sup>. Compute the effectiveness and engine efficiency for the turbine.

**39.** Saturated steam at 100 psia is throttled in a valve to a pressure of 20 psia. Compute the loss of available energy.

### Symbols

<i>a</i>	availability of heat
<i>b</i>	availability function $b = h - T_0 s$
<i>c</i>	heat capacity
<i>C</i>	constant
<i>ε</i>	effectiveness
<i>F</i>	degrees Fahrenheit
<i>h</i>	specific enthalpy
<i>HP</i>	high pressure
hp-hr	horsepower hour
<i>I</i>	irreversibilities
<i>J</i>	Joules equivalent
<i>KE</i>	kinetic energy
kwhr	kilowatthour
<i>LP</i>	low pressure
<i>m</i>	mass, also, mass flow rate
<i>p</i>	pressure
<i>PE</i>	potential energy
<i>r</i>	ratio
<i>R</i>	degrees Rankine
<i>s</i>	specific entropy
<i>S</i>	entropy
<i>t</i>	thermodynamic temperature
<i>T</i>	absolute thermodynamic temperature
<i>u</i>	specific internal energy

$V$	velocity, also, volume
$v$	specific volume
$Q$	heat
$W$	work
$x$	quality
$y$	ratio of extracted steam to total steam flow
$z$	height, also, ratio of mass flow rate of mercury to that of steam in the binary cycle
$  $	absolute value sign
$\approx$	approaches equality

#### Greek Letters

$\Delta$	(delta)	difference
$\eta_t$	(eta)	thermal efficiency
$\eta_c$	(eta)	compression efficiency
$\eta_e$	(eta)	expansion (engine) efficiency
$\Sigma$	(sigma)	summation

#### Subscripts

$A$	added
act	actual
$c$	compression (efficiency)
$e$	engine or expansion (efficiency)
$f$	saturated liquid
$fg$	difference between saturated liquid and saturated vapor
isen	isentropic
$p$	pressure
$R$	rejected
rev	reversible
$t$	thermal (efficiency)
$W$	work
0	atmospheric conditions

#### Suggested References

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- 3 DARRIEUS, G. The Rational Definition of Steam Turbine Efficiencies, *Engineering*, **130** (No. 3373), 283-285 (Sept. 5, 1930)
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## CHAPTER XIII

### POWER CYCLES—GAS

For the production of power in amounts of 50,000 and 100,000 kw, the large central station with a vapor (steam) cycle is the universal system. When the power requirements are small (less than 10,000 kw) or when light weight is demanded or variable-speed operation is required, the internal-combustion engine is the preferred source of power. However, development work now in progress on gas turbines forecasts that this form of prime mover may well prove to be an active competitor of both steam and the internal-combustion engine.

**13-1. Thermodynamic Relationships for Processes and Cycles.** It may prove helpful to summarize here the equations that will be used throughout this chapter. The First Law equations<sup>1</sup> are valid for either reversible or irreversible processes:

$$Q - W = \Delta u]_{\text{nonflow}} \quad (3-7c)$$

$$Q - W = \Delta h]_{\text{flow}} \quad (3-13b)$$

Most engineering processes do not involve combinations of both work and heat. For these processes

$$Q = \Delta u]_{W=0}^{\text{nonflow}} \quad Q = \Delta h]_{W=0}^{\text{flow}}$$

and

$$W = -\Delta u]_{Q=0}^{\text{nonflow}} \quad W = -\Delta h]_{Q=0}^{\text{flow}}$$

The perfect-gas relationships will simplify the presentation in later articles:

$$\Delta u = \int c_v dT \quad (7-7)$$

$$\Delta h = \int c_p dT \quad (7-8)$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \quad (8-10, 8-11)$$

$$p_1 v_1^\gamma = p_2 v_2^\gamma = C \quad (8-9)$$

<sup>1</sup> The same assumption is made as in Chap. XII: insignificant change occurs in kinetic or potential energy at the boundary (end points) for each process.

And for isothermal processes of a perfect gas, the change in internal energy and enthalpy is zero; therefore, for flow or nonflow processes,

$$Q = W]_T$$

If the isothermal flow or nonflow process is reversible,

$$W_{\text{rev}}]_T = RT \ln \frac{v_2}{v_1} \quad (8-7b)$$

while for other reversible nonflow processes of a perfect gas

$$W_{\text{rev}} = \left[ \frac{p_2 v_2 - p_1 v_1}{1 - n} \right]_{\text{nonflow}} = \left[ \frac{R(T_2 - T_1)}{1 - n} \right]_{\text{nonflow}} \quad (8-12)$$

The work of the reversible flow process is  $n$  times the values in Eq. (8-12) The transfer of heat for any fluid is evaluated by

$$Q_{\text{rev}} = \int T ds \quad (5-5)$$

$$Q_{\text{rev}} = \int c_x dT \quad (4-5)$$

The work of the cycle (for any fluid) is

$$\Sigma W = Q_A + Q_R$$

$$\Sigma W = \eta_i Q_A$$

and, also,

$$\Sigma W = W_{\text{process 1}} + W_{\text{process 2}} + \dots$$

The thermal efficiency is

$$\eta_i = \frac{\Sigma W}{Q_A} \quad (3-20)$$

**13-2. Definitions.** Only flow processes appeared in the cycles discussed in Chap XII, while here emphasis will be mainly on cycles made up of nonflow processes. In these cycles the process efficiencies for expansion and compression will be defined by the same equations as before (Art 12-1). But the nonflow processes will be executed in a system contained by a piston and cylinder, and the positive and negative work quantities cannot, in the real machine, be readily separated. For this reason the work ratio is not used, but, instead, a new parameter of performance is introduced—the mean effective pressure<sup>1</sup> (abbreviated mep). The mep, like the work ratio, is an index that relates the size of the equipment to the work output. It is equal to

<sup>1</sup> See Arts 4-5 and 8-9c

the net work divided by the maximum change in volume of the system during one complete cycle:

$$\text{mep} = \frac{\Sigma W}{V_{\max} - V_{\min}} \Big|_{\text{cy}} \quad (13-1a)$$

With  $W$  in ft lb<sub>f</sub> and  $V$  in ft<sup>3</sup>, the dimension for mep is that of pressure, lb<sub>f</sub> ft<sup>-2</sup>. The denominator of Eq (13-1a) is the volume swept by the piston in either its outward or inward travel, and therefore this volume is called the *piston displacement* ( $V_D$ ). Then the mep can be imagined to be a constant pressure which, by acting on a piston throughout one displacement, can deliver the net work of the cycle

$$\text{mep} = \frac{\Sigma W}{V_D} \quad (13-1b)$$

The mep can be either the *indicated* mean effective pressure (imep) or the *brake* mean effective pressure (bmep). The imep is found by measuring the indicated work done by the fluid in one cycle and dividing this quantity by the piston displacement. The bmep is found by measuring the brake work delivered by the machine (which is less than the indicated work because of the presence of friction) and dividing by the piston displacement.

One objective of the engineer is to use cycles that have high thermal efficiencies and also high mean effective pressures. A high thermal efficiency<sup>1</sup> is a factor contributing to low cost of operation while a high mep is a factor contributing toward a smaller size engine and therefore a lower initial cost.

The *expansion ratio* of the cycle is a volume ratio

$$r_v = \frac{V_{\max}}{V_{\min}} \Big|_{\text{cy}} \quad (13-2a)$$

but this is also the *compression ratio* since the piston will retrace its steps in completing the cycle. These ratios are also applied to an individual process in the cycle.

$$r_v = \frac{V_{\max}}{V_{\min}} \Big|_{\text{process}} \quad (13-2b)$$

<sup>1</sup> But an engine with high thermal efficiency may also demand a specialized and costly fuel, and power might be more cheaply obtained by using a cycle with lower efficiency and cheaper fuel. A low mep can also be circumvented by operating the cycle at high speed (if this is possible) since power is but the time rate of doing work.

The *pressure ratio*, like the expansion or compression ratio, will be, in this chapter, a number always greater than unity:

$$r_p = \left. \frac{p_{\max}}{p_{\min}} \right]_{\text{process or cycle}} \quad (13-3)$$

**13-3. The Carnot Cycle (1824).** The changes in state of a gas, in passing through the processes of a Carnot cycle, are illustrated in Fig. 13-1. Comparison of Fig. 13-1 with Fig. 12-2 shows that the  $Ts$  diagram is the same for either gas or vapor but that the  $pv$  diagrams differ. The difference is that the isothermal processes for a gas are not constant-pressure processes, for this reason, no simplification is possible by using flow processes for the cycle. But a cycle of nonflow processes has the advantage of compactness; for this reason the performance of such a cycle will be investigated

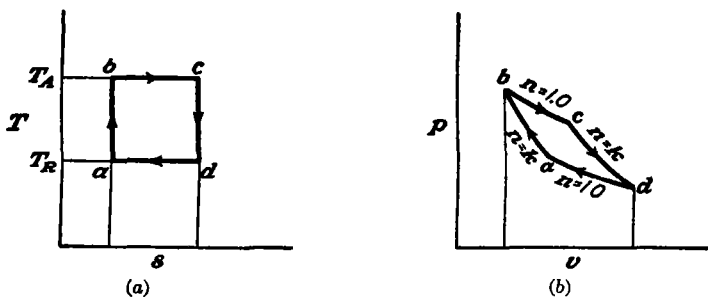


Fig 13-1 The Carnot cycle (a) For any fluid (b) For a gas

Consider a perfect gas to be the working fluid for a Carnot cycle that contains only nonflow processes. To this cycle, illustrated in Fig. 13-1, the relationships of Art. 13-1 can be applied:

$$Q_{A\text{rev}} = W_{bc} = RT_A \ln \frac{v_c}{v_b} = T_A \Delta s_{bc}$$

$$Q_{R\text{rev}} = W_{da} = RT_R \ln \frac{v_a}{v_d} = T_R \Delta s_{da}$$

Therefore, since  $\Delta s_{bc} = -\Delta s_{da}$

$$\frac{v_c}{v_b} = \frac{v_d}{v_a}$$

and

$$\begin{aligned} \Sigma W &= Q_A + Q_R \\ \Sigma W_{\text{rev}} &= R(T_A - T_R) \ln \frac{v_c}{v_b} \\ \eta_t &= \frac{\Sigma W}{Q_A} = \frac{R(T_A - T_R) \ln (v_c/v_b)}{RT_A \ln (v_c/v_b)} = \frac{T_A - T_R}{T_A} \end{aligned}$$

The mean effective pressure is equal to

$$\text{mep} = \frac{\Sigma W}{V_{\max} - V_{\min}} = \frac{R(T_A - T_R) \ln (v_c/v_b)}{v_d - v_b} \quad (13-4)$$

The thermal efficiency can also be expressed in terms of the isentropic compression (or expansion) ratio (but not the over-all compression ratio):

$$\eta_t = \frac{T_A - T_R}{T_A} = 1 - \frac{T_c}{T_b}$$

Substituting Eqs. (8-10) and (13-2b),

$$\eta_t = 1 - \frac{1}{r_v^{k-1}} \quad (13-5)$$

where  $r_v$  = isentropic compression (or expansion) ratio  $= \frac{v_a}{v_b} = \frac{v_d}{v_c}$

**Example 1:** A Carnot cycle, using air as the working fluid, operates between temperatures of 80 and 780 F. The pressure at the start of isothermal compression is 14.7 psia, and 195 Btu of heat are added to the cycle per pound mass of air. Determine the thermal efficiency, net work, compression ratio, and imep for the cycle.

**Solution:** The thermal efficiency is

$$\eta_t = \frac{T_A - T_R}{T_A} = \frac{780 - 80}{780 + 459.7} = 0.565, \text{ or } 56.5 \text{ per cent} \quad \text{Ans.}$$

The net work is

$$\Sigma W = \eta_t Q_A = 0.565(195) = 110 \text{ Btu/lb}_m \text{ air} \quad \text{Ans.}$$

The volumes at states *abcd* will next be found:

*State d*

$$p_d = 14.7 \text{ psia}$$

$$t_d = 80 \text{ F}$$

$$v_d = \frac{RT}{p} = \frac{10.73(540)}{29(14.7)} \\ = 13.6 \text{ ft}^3/\text{lb}_m$$

*State a*

$$t_a = 80 \text{ F}$$

$$Q_R = RT_a \ln \frac{v_a}{v_d}$$

(from state *d* to *a*)

$$-(195 - 110) = \frac{1.986}{29} (540) \ln \frac{v_a}{v_d}$$

$$v_a = 1.36 \text{ ft}^3/\text{lb}_m$$

*State b*

$$t_b = 780 \text{ F}$$

$$\frac{T_b}{T_a} = \left(\frac{v_a}{v_b}\right)^{k-1}$$

$$v_b = 0.170 \text{ ft}^3/\text{lb}_m$$

*State c*

$$\frac{v_c}{v_b} = \frac{v_d}{v_a}$$

$$v_c = 1.70 \text{ ft}^3/\text{lb}_m$$

With these values the cycle compression or expansion ratio is

$$r_v = \frac{V_{\max}}{V_{\min}} = \frac{13.6}{0.170} = 80 \quad Ans$$

The isothermal expansion or compression ratio is

$$r_v = \frac{V_c \text{ or } d}{V_b \text{ or } a} = \frac{1.70}{0.170} = 10$$

The isentropic expansion or compression ratio is

$$r_v = \frac{V_a \text{ or } d}{V_b \text{ or } c} = \frac{1.36}{0.170} = 8$$

The imep is

$$\text{imep} = \frac{\Sigma W}{144(V_{\max} - V_{\min})} = \frac{110(778)}{144(13.6 - 0.170)} = 41.5 \text{ lb/in}^2 \quad Ans$$

The imep of a modern engine is over 100 lb/in<sup>2</sup>, therefore, the above value of 41.5 lb/in<sup>2</sup> is quite low. Moreover, the pressures in this Carnot cycle are quite high because of the extremely high compression ratio

$$\begin{aligned} p_a v_a &= p_d v_d & p_a &= p_d \left( \frac{v_d}{v_a} \right) = 147 \text{ psia} \\ p_b v_b^k &= p_a v_a^k & p_b &= p_a \left( \frac{v_a}{v_b} \right)^k = 2,720 \text{ psia} \\ p_c v_c &= p_b v_b & p_c &= p_b \left( \frac{v_b}{v_c} \right) = 272 \text{ psia} \end{aligned}$$

When the Carnot cycle includes a vapor and flow processes, it becomes a practical cycle for power generation although other cycles are more desirable (Chap. XII). But the Carnot cycle for a gas and nonflow processes is quite impractical because heat must be transferred, to and from the working fluid, through the walls of the engine. Such a method of heat transfer limits the operation of the engine to extremely slow speeds. Moreover, the metal surfaces of the engine must attain and exceed the highest temperature of the cycle if heat is to be transferred at a finite rate through the walls to the working fluid, therefore, the maximum temperature of the cycle would be limited by metallurgical, if not also by lubrication, problems.

**13-4. The Combustion Engine.** The practical method for copying the processes of the nonflow cycle is to burn a fuel internally within the engine and so dispense with the necessity for a heat-transfer process. The temperature attained in the internal-combustion process can be extremely high, far above the melting temperatures of metals, because succeeding processes, which are at lower temperatures, will

cool<sup>1</sup> the parts of the engine. In 1893, Dr Rudolph Diesel tried to simulate the Carnot cycle by gradually injecting a fuel during the expansion stroke (bc Fig 13-1). He reasoned that fuel introduced at this point of the cycle should spontaneously ignite since the air had been compressed to a high temperature. Then, as the piston descended on the working stroke and the temperature tended to fall, fuel could be continuously injected and burned at a rate such that the process would be isothermal. The other processes of the Carnot cycle would then follow in the usual order. Dr Diesel soon found that isothermal expansion and isothermal compression could not be accomplished<sup>2</sup> and

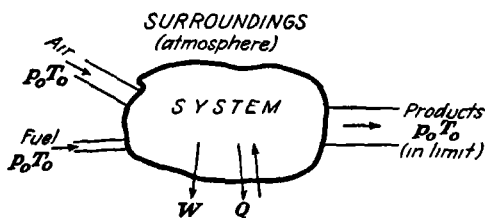


FIG 13-2 Thermodynamic system for the internal combustion engine.

that the high pressures that would result from the double compression, isothermal followed by isentropic compression, were undesirable.

Moreover, the attainment of the Carnot processes is neither necessary nor desirable in an internal-combustion engine. Consider that this engine does not involve a cycle, but, rather, the over-all system is a process. Thus, in Fig 13-2, air and fuel enter while the products of combustion leave the system, the maximum work for a system similar to this was evaluated in Art 11-15 and found to be equal to the free-energy change of the flow stream. The internal-combustion engine would deliver this maximum amount of work, without regard for the Carnot processes, if the processes selected for the engine were all reversible. No practical means are known of conducting the combustion<sup>3</sup> process in a reversible manner.

A theoretical means, however, can be imagined. Consider that the combustion process at equilibrium contains both mixture<sup>4</sup> and products in definite proportions.

<sup>1</sup> A stagnant layer of fluid surrounds the working fluid at all times, and therefore a high temperature gradient exists between the walls and the fluid, too, the metal surfaces are externally cooled by water or air.

<sup>2</sup> It is interesting to note that the isothermal compression was to be attained by injecting water into the working fluid.

<sup>3</sup> But, in the storage battery, a chemical reaction could be conducted in essentially a reversible manner.

<sup>4</sup> The fuel must be a simple substance such as gaseous carbon and not a complex compound.



and in amounts predicted by the equilibrium constant. When the temperature of the equilibrium mixture is raised, the equilibrium shifts and the degree of completion of the reaction diminishes, therefore, a state will exist at an *extremely high* temperature where the mixture can exist in equilibrium with an infinitesimally small proportion of products. A theoretical manner for conducting a reversible combustion process is now apparent. The mixture can be isentropically compressed to the high temperature where essentially no reaction occurs. (It is assumed that the speed of the compression process is extremely swift, and therefore reaction does not begin during the compression, or else a negative catalyst is present.) Then, the mixture can be slowly and isentropically expanded, as the temperature falls, reaction reversibly occurs, and at each temperature level of the expansion a greater and greater amount of products will be formed. In this sequence of processes (at constant<sup>1</sup> entropy) chemical reaction can be conceived to be reversibly executed although, of course, not at constant temperature.

The isentropic expansion can be continued until the products reach a temperature<sup>2</sup> equal to that of the original mixture (and this is the temperature of the atmosphere). But, because of the change in volume that may accompany chemical reaction, the pressure of the products may be greater, equal, or less than the initial pressure of the mixture (which is also the pressure of the atmosphere), if the pressure is greater, the products can be isothermally expanded while heat is reversibly *supplied* by the atmosphere, if the pressure is less, the products can be isothermally compressed while heat is reversibly *rejected* to the atmosphere. In the isothermal heat-transfer process, the entropy of the system will be either increased or decreased depending upon the direction<sup>3</sup> of the flow of heat.

The work of the system for the series of processes will be that obtained in the isentropic expansion (reaction) process plus (or minus) that work obtained (or added) in the isothermal process and minus that work originally supplied for the isentropic compression process. The net work obtained (that is, work other than to push aside the atmosphere) must be equal in amount to the decrease in free energy [Eq. (11-15)]

Although the processes of a reversible internal-combustion engine bear no resemblance to the processes of the Carnot cycle, the same conclusions are evident for either system. *For the highest thermal efficiency, the combustion engine and the thermodynamic cycle must operate between the highest and lowest temperature that can be attained.* In a cycle, heat should be added at the highest possible temperature; in an internal-combustion engine, combustion should begin at the highest possible temperature, for then the irreversibility of the chemical reaction is reduced. Moreover, in both the cycle and the combustion engine, expansion should proceed to the lowest possible temperature in order to obtain the maximum amount of work. Because of these

<sup>1</sup> The entropy is constant because both processes are reversible and adiabatic.

<sup>2</sup> Or a reversible path can be devised after expanding to the mixture pressure (which is the pressure of the atmosphere).

<sup>3</sup> The direction of the heat transfer can be predicted by comparing the entropy of the mixture to that of the products. See Table XIII (Appendix) and Art. 11-15.

similarities, the internal-combustion engine can be analyzed as if it were a cycle by assuming that the combustion process is equivalent to a transfer of heat and that no change in composition is undergone by the fluid. Such an analysis, of course, will not be exact, but certain fundamental relationships can be simply obtained that are of real interest (Arts 13-6 to 13-11)

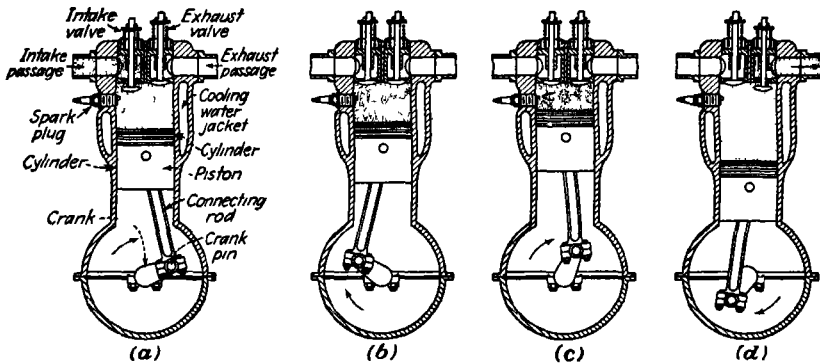


FIG 13-3 The sequence of operations for the spark-ignition (SI) engine (a) Intake stroke (b) Compression stroke (c) Expansion stroke (d) Exhaust stroke.

**13-5. The Otto Engine (1862–1876).** In 1862 Beau de Rochas proposed for the internal-combustion engine a sequence of operations that is, even today, typical of most spark-ignition engines.

- 1 An *intake stroke* to draw a combustible mixture into the cylinder of the engine (Fig 13-3a),
- 2 A *compression stroke* to raise the temperature of the mixture (Fig 13-3b),
- 3 Ignition and combustion of the mixture at the end of the compression stroke with the consequent liberation of energy raising the temperature and pressure of the gases as the piston descends downward on the *expansion or power stroke* (Fig 13-3c),
- 4 An *exhaust stroke* to sweep the cylinder free of the burned gases (Fig 13-3d).

In 1876, Otto, a German engineer, using the principles of Beau de Rochas, built an engine that became highly successful, and the name of the cycle of events gradually became known as the Otto cycle

The pressures experienced in the spark-ignition (abbreviated SI) engine at full load (at wide-open throttle) are shown in Fig 13-4a. During the intake stroke the pressure in the cylinder is closely atmospheric, being less only because of fluid friction. On the following

stroke, the mixture of gasoline vapor and air is compressed to the highest temperature that can be attained without spontaneous ignition of the mixture (Compression ratios of 6 to 8 are usual) A spark then ignites the mixture, which rapidly burns while the piston comes to rest at the top dead-center position of the crank mechanism During this period of little movement of the piston, combustion of the mixture takes place at essentially constant volume (as proposed by de Rochas)<sup>1</sup> The increase in temperature from burning the fuel causes the pressure to increase, and thus high pressures are available to drive the piston downward on the power stroke. Although, if the greatest amount of

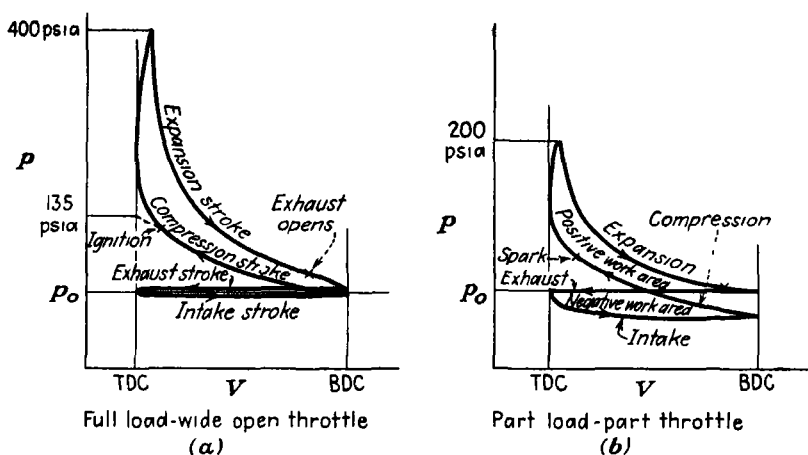


FIG 13-4 Pressure-volume ( $pV$ ) diagrams for the spark-ignition (SI) engine

work is to be obtained, expansion should proceed to atmospheric pressure, such a complete expansion would require a higher expansion ratio than compression ratio Too, the size of the engine would be large For these reasons, the exhaust valve is opened before the end of the expansion stroke to allow the pressure to drop to atmospheric before the exhaust stroke is begun The exhaust stroke then purges the remaining gas from the cylinder with the exception of the small amount contained within the clearance space (combustion chamber)

In the SI engine, a spark can ignite only a combustible mixture. A fairly definite relationship of fuel and air (approximately 12 to 16 parts of air to 1 part of fuel by mass) must therefore be present in all parts of the chamber at all loads if a flame is to travel through the

<sup>1</sup> De Rochas also suggested that the spark plug would be unnecessary because the fuel-air mixture would spontaneously ignite at the end of the compression stroke

mixture The turning effort applied to the crankshaft depends on the mass of mixture burned in the cylinder, and this effort is controlled by restricting the amount of mixture (but not primarily the air-fuel ratio) entering the cylinder on the intake stroke. This load control is accomplished by using a valve, called the *throttle*, to obstruct the passageway that leads to the cylinder. On the intake stroke, if the throttle is not open, the pressure in the cylinder is reduced below atmospheric, and a reduced mass of mixture will enter the cylinder with correspondingly lower compression pressures and combustion pressures (Fig 13-4b). Note that the work obtained from the partially loaded engine is reduced, not only because less fuel (and air) is inducted than at full load, but also because the negative work of the engine cycle is increased. The negative work area of Fig 13-4b is a result of the wasteful throttling process that is used as the method of governing.

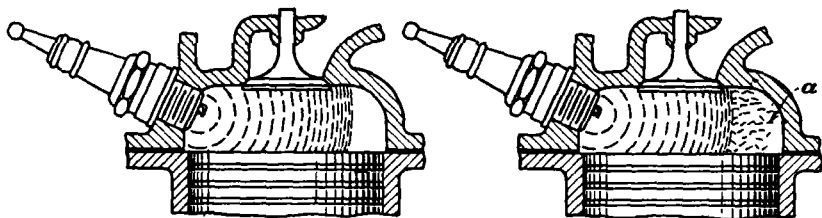


FIG 13-5 Detonation in the SI engine

Although combustion of the fuel should take place at the highest possible temperature, the Otto cycle is restricted to relatively low compression ratios. The reason for this can be understood by studying Fig 13-5. After passage of the ignition spark, a flame sweeps out from the spark plug and transforms the mixture into products of combustion. The energy released will be proportional to the mass of charge burned, and this release can be accomplished in an orderly manner by properly controlling the speed of the flame. As the flame progresses across the chamber, the unburned mixture is compressed, and its temperature therefore increases. If the temperature should reach a certain critical value, the unburned mixture will ignite, as at *a* in Fig. 13-5, without depending on the advancing flame. There will then result an energy release sufficient to produce a momentary high and localized pressure that causes an audible “knock” to be heard. The *knock*, or *detonation*, is caused by the almost instantaneous explosion of a part of the mixture. The resulting impact on the engine structure may cause failure, for this reason the compression ratio of the Otto engine must be kept at a low value (or else expensive fuels, which can resist compression

ignition, are required). In other words, combustion of the fuel in the Otto engine must be fast but not explosive because no mechanical structure can long resist impact

**13-6. Actual and Air-standard Processes.** The actual process in an engine is complicated by many variables, among which should be mentioned the following: (a) The fuel-air ratio may not be constant, (b) the characteristics of the available fuels are variable; (c) the composition of the fuel-air mixture changes as combustion takes place; (d) the heat-capacity values of the operating medium vary greatly with temperature changes; (e) dissociation of the gases taking part in combustion influences maximum temperatures and alters the character of the expansion curve; (f) heat transfers actually occur during each

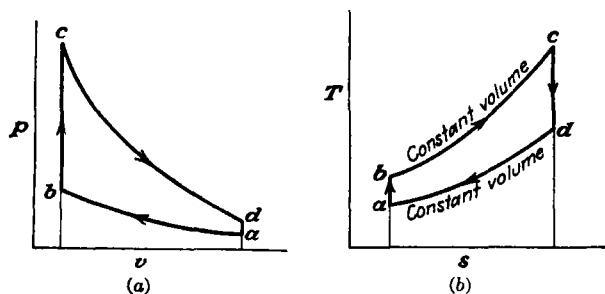


FIG 13-6 Air standard Otto cycle

process; (g) the burned clearance gases dilute the fresh charge, and (h) there is throttling of the charge during induction and exhaust

Despite these factors, a simplified analysis of a hypothetical cycle can be used advantageously to show the effect of changing operating conditions, to indicate maximum performance, and to furnish a basis for making approximations that more closely bring the cycle to actual conditions. The hypothetical cycle presupposes that air alone is the working fluid; hence, it is known as the *air-standard cycle*. Heat, it is assumed, can be directly supplied to or rejected from the cycle and, to simplify the analysis further, loss of heat is ignored while the heat capacity of the fluid is usually considered to be constant. Naturally, the resulting cycle is far removed from the actual case, but the factors affecting the performance or the efficiency are essentially the same for both the actual engine and this theoretical cycle

More exact analyses are reserved for more specialized textbooks <sup>1</sup>

**13-7. The Otto Cycle.** A hypothetical cycle for the Otto engine can be patterned from the  $p$ - $v$  diagram of Fig 13-4. The compression

<sup>1</sup> See reference 1

and expansion processes are, ideally, isentropic processes. Combustion and "blowdown" of the exhaust, which occur closely at constant volume of the engine, will be arbitrarily made into constant specific-volume processes, and, therefore, these processes are the heat-transfer processes for the proposed cycle. The resulting  $pv$  diagram (Fig. 13-6a) is quite similar to the  $pV$  diagram of Fig. 13-4. The  $Ts$  diagram (Fig. 13-6b) is constructed for the same processes:

1. Isentropic compression  $ab$ ,
2. Constant-volume addition of heat  $bc$ ,
3. Isentropic expansion  $cd$ ,
4. Constant-volume rejection of heat  $da$ .

For this cycle, per unit mass of air,

$$\begin{aligned} Q_{A,\text{rev}} &= c_v(T_c - T_b) \\ Q_{R,\text{rev}} &= c_v(T_a - T_d) \\ \eta_t &= \frac{Q_A + Q_R}{Q_A} = 1 - \frac{T_d - T_a}{T_c - T_b} \end{aligned} \quad (a)$$

and, since compression and expansion ratios are equal,

$$\frac{T_a}{T_b} = \left(\frac{v_b}{v_a}\right)^{k-1} = \left(\frac{v_c}{v_d}\right)^{k-1} = \frac{T_d}{T_c} \quad (b)$$

or

$$\frac{T_d}{T_a} = \frac{T_c}{T_b}$$

Subtracting unity from each side of the above equation,

$$\frac{T_d}{T_a} - 1 = \frac{T_c}{T_b} - 1 \quad \text{or} \quad \frac{T_d - T_a}{T_a} = \frac{T_c - T_b}{T_b} \quad (c)$$

Substituting Eq (c) in Eq (a),

$$\eta_t = 1 - \frac{T_a}{T_b}$$

And from Eqs. (b) and (13-2a)

$$\eta_t = 1 - \left(\frac{v_b}{v_a}\right)^{k-1} = 1 - \frac{1}{r^{\frac{k-1}{\gamma}}} \quad (13-5)$$

Note that the thermal efficiency of the Otto cycle is equal to that of a Carnot cycle that has the same *isentropic* compression ratio (although the over-all compression ratio of the Carnot is higher than that for the Otto cycle)

Equation (13-5) proves that the thermal efficiency of the Otto cycle (or of the Carnot cycle) is a function of the isentropic compression (or expansion) ratio and that it is influenced by the properties of the fluid. Thus, the Otto cycle with helium ( $k = 1.6$ ) as the working fluid has a higher thermal efficiency than when air ( $k = 1.4$ ) is used (comparison, of course, is made at the same  $r_v$ ). Too, the efficiency of the theoretical cycle is independent of the load (which is varied by varying the quantity of heat added to the cycle).

The thermal efficiency of the real engine is much less than that predicted by the air-standard analysis (about one-half). In Fig 13-7 is pictured a more exact analysis, by Goodenough and Baker,<sup>1</sup> based upon the following premises

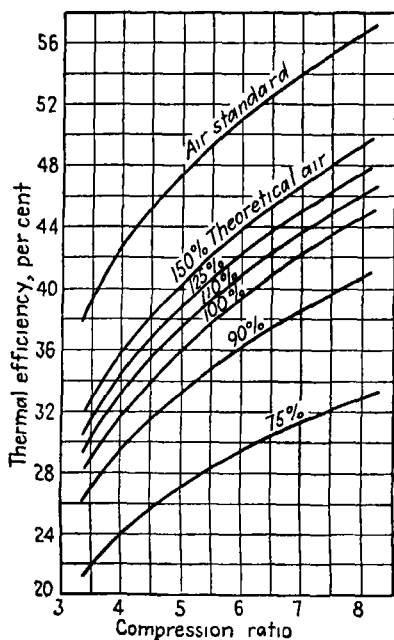


FIG 13-7 Effects of compression ratio and mixture strength upon thermal efficiency of the Otto cycle (from reference 2)

- 1 The mixture consists of air, gasoline vapor, and exhaust products left in the clearance space,
- 2 The mixture may not be chemically correct, a deficiency of air or fuel may be present,
- 3 The heat capacities are not constant;
- 4 The mixture during combustion is in chemical equilibrium
- 5 The pressure during the intake stroke (or the exhaust stroke) is 14.7 psia,
- 6 All processes are adiabatic,
- 7 Combustion occurs at constant volume

Although the heat-capacity-dissociation data used by Goodenough and Baker in 1927 are somewhat inaccurate in the light of modern data, still, the results obtained are very useful in indicating optimum magnitudes and variations under different variables of operation

<sup>1</sup> See reference 2

**Example 2:** An Otto cycle using air has a compression ratio of 8. At the start of the compression process (point *a* in Fig. 13-6) the temperature is 540 R, and the pressure is 14.7 psia. Heat is supplied at the rate of 1280 Btu/lb<sub>m</sub> of air. Determine the thermal efficiency, net work, imep, and the pressure and temperature at key points of the cycle.

**Solution:** From Eq. (13-5)

$$\eta_t = 1 - \frac{1}{r_v^{k-1}} = 1 - \frac{1}{8^{1.4-1}} = 0.565, \text{ or } 56.5 \text{ per cent} \quad \text{Ans}$$

This answer is equal to that in Example 1, the net work must also be the same since the same amount of heat was added.

$$\Sigma W = \eta_t Q_A = 0.565(1280) = 723 \text{ Btu/lb}_m \text{ air} \quad \text{Ans}$$

**State a**

$$\begin{aligned} p_a &= 14.7 \text{ psia} & v_a &= \frac{RT}{p} = \frac{10.73(540)}{29(14.7)} \\ T_a &= 540 \text{ R} & v_a &= 13.6 \text{ ft}^3/\text{lb}_m \end{aligned}$$

**State b**

$$\begin{aligned} \frac{p_b}{p_a} &= \left(\frac{v_a}{v_b}\right)^{k-1} & \frac{T_b}{T_a} &= \left(\frac{v_a}{v_b}\right)^{k-1} & \frac{v_a}{v_b} &= r_v = 8 \\ p_b &= p_a(r_v)^{k-1} & T_b &= T_a(r_v)^{k-1} & v_b &= 1.70 \text{ ft}^3/\text{lb}_m \\ p_b &= 14.7(8)^{0.4} & T_b &= 540(8)^{0.4} & & \\ p_b &= 270 \text{ psia} & T_b &= 1240 \text{ R} & & \end{aligned}$$

**State c**

$$Q_{bc} = mc_v \Delta T$$

and from Table VI (Appendix)

$$\begin{aligned} c_v &= 0.17 \text{ Btu/lb}_m \text{ R} \\ 1280 &= 0.17(\Delta t) \\ \Delta t &= 7500 \text{ R} \\ T_c &= T_b + \Delta t = 1240 + 7500 = 8740 \text{ R} \end{aligned}$$

The volumes at *b* and *c* are equal, therefore,

$$\frac{p_c}{p_b} = \frac{T_c}{T_b} \quad p_c = 270 \left(\frac{8740}{1240}\right) = 1900 \text{ psia}$$

**State d**

$$\frac{T_d}{T_c} = \left(\frac{v_c}{v_d}\right)^{k-1}$$

Since the volumes at *a* and *d* are equal,

$$\begin{aligned} T_d &= T_c \left(\frac{1}{r_v}\right)^{k-1} & \frac{p_d}{p_a} &= \frac{T_d}{T_a} \\ T_d &= 8740 \left(\frac{1}{8}\right)^{0.4} & p_d &= p_a \left(\frac{T_d}{T_a}\right) \\ T_d &= 3800 \text{ R} & p_d &= 14.7 \left(\frac{3800}{540}\right) \\ & & p_d &= 104 \text{ psia} \end{aligned}$$

The imep is

$$\text{imep} = \frac{\Sigma W}{V_D} = \frac{(723 \text{ Btu/lb}_m)(778 \text{ ft lb/Btu})}{(144 \text{ in}^3/\text{ft}^3)(13.6 - 1.7)} = 327 \text{ lb}_f/\text{in}^2 \quad \text{Ans.}$$



Note that the imep for this Otto cycle is far greater than that for the Carnot cycle analyzed in Example 1, although the maximum pressure in the Otto cycle is less than in the Carnot cycle. It might be argued that the Otto cycle experienced a higher maximum temperature than did the Carnot and that therefore the comparison is unfair. This is a valid objection, but it should be remembered that in the real engine a combustion process is to be used to generate the temperature. The real engine is more sensitive to high pressures than it is to high temperatures when both are of brief duration, thus, this example shows the Otto cycle to be preferable to the Carnot cycle when pressure is the limiting factor.

**13-8. The Diesel Engine (1893).** The failure of Dr. Diesel's first engine (Art 13-4) caused him to abandon, as ideals, the impractical isothermal processes in favor of adiabatic compression and expansion processes. The successful diesel engine embodied the following events:

- 1 An *intake stroke* to induct air alone into the cylinder without wasteful throttling;
- 2 A *compression stroke* to raise the air to a high temperature, a temperature higher than the ignition point of the fuel;
- 3 Injection of the fuel during the first part of the expansion stroke at a rate such that combustion maintains the pressure constant, followed by expansion to the initial volume of the cylinder
- 4 An *exhaust stroke* to remove the burned gases from the cylinder

The success of the diesel engine can be attributed to the fact that only air is compressed in the engine, therefore, the compression ratio can be much higher than that of the Otto engine, which compresses a combustible mixture.

Typical pressures encountered in the compression-ignition (abbreviated CI) engine at full load are shown in Fig. 13-8. During the intake stroke, air alone is drawn into the cylinder, and the pressure is closely atmospheric. The air is then compressed to a pressure of 350 to 500 psia (compression ratios of 12 to 18 are in use) before the fuel is injected into the high-temperature air. An early method of injecting the fuel was to use a blast of compressed air to carry the fuel into the engine through a small orifice called the *nozzle*. This method gave good atomization and good control of the combustion process, as can be recognized in Fig. 13-8a, which shows, closely, a constant-pressure combustion. However, *air injection* is rarely used because an air compressor becomes a necessary and expensive auxiliary. The modern method of injection is to compress and spray the fuel alone into the cylinder through the nozzle and depend upon a high injection pressure (2,000 psia) for atomizing the fuel. If the injection period is long and the speed of the engine is slow, indicator cards similar to Fig. 13-8a can

be obtained. However, although Dr. Diesel insisted upon operating his engines with essentially constant-pressure combustion, constant-volume combustion is thermodynamically more desirable<sup>1</sup> because the chemical energy is liberated at the very beginning of the expansion stroke. For this reason, the indicator cards of modern engines resemble Fig 13-8b; here the first part of the fuel to be injected burns essentially at constant volume while the remainder burns essentially at constant pressure

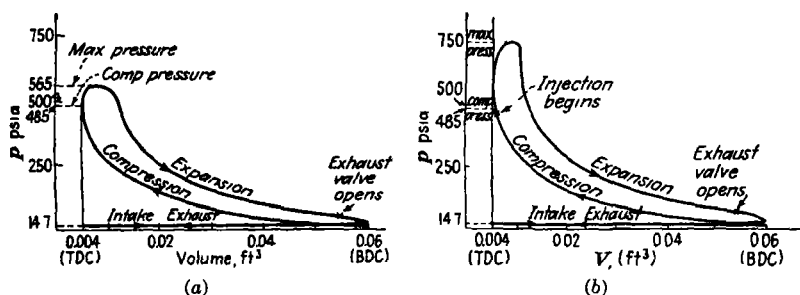


FIG 13-8 Pressure-volume (pV) diagram for the compression-ignition (CI) engine (a) Air injection (or late and slow mechanical injection) (b) Solid (mechanical) injection

The CI engine is not completely free from “knock” or detonation. When the first particles of liquid fuel are injected into the hot compressed air, an interval of time will elapse while atomization, vaporization, distribution, and initial chemical reaction take place. During this *delay* period, more and more fuel enters the chamber. Because of this accumulation of fuel, when combustion does begin the reaction tends to be uncontrollably fast, and therefore a high localized pressure rise is experienced. This violent pressure rise is an impact on the parts of the engine that can be quite destructive. Since the diesel engine has a high pressure before combustion, any additional pressure rise from combustion only increases the design troubles, probably for this reason, Dr. Diesel insisted upon constant pressure as the desideratum for his engine.

The load control of the CI engine is a simple matter because only the quantity of fuel need be regulated. Thus, at full load it is desired to inject a quantity of fuel such that all the air in the cylinder can be burned. Practically, this limit cannot be reached because it is not possible for the localized fuel spray to find all the air, rich and lean regions abound, and the engine exhaust gas is colored in appearance and pungent in odor. At part load, only a fraction of the full-load

<sup>1</sup> See Art. 13-11

fuel quantity is injected. In localized regions, combustion of the fuel occurs at ratios of air to fuel of about 15 to 1, although the over-all air-fuel ratio is much higher than this. Thus, at full output of the engine, most of the air is used for reaction, at part load only a fraction of the air need be combined with the fuel, and, because of the localized combustion, the intake-air process need not be throttled at any time. Because of this free induction of air, the efficiency of the CI engine is not penalized at part loads by a wasteful throttling process such as that used by the SI engine. (Whether or not the fuel in the CI engine is throttled is unimportant because the work spent in pumping the liquid is relatively small when compared to that for a gas.)

**13-9. The Diesel Cycle.** A hypothetical cycle for the diesel engine can be patterned after the  $pV$  diagram of Fig. 13-8a in the same manner

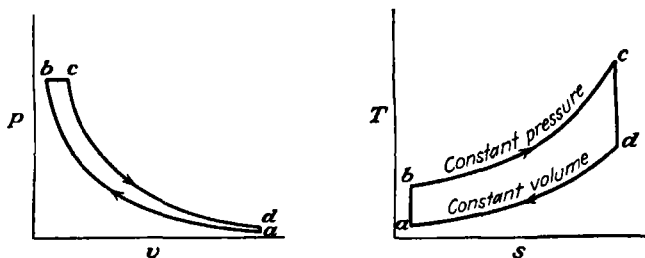


FIG. 13-9 Air standard Diesel cycle

that was followed for the Otto cycle in Art. 13-7. The compression and expansion processes become isentropic processes in the ideal cycle, the constant-pressure combustion process becomes a constant-pressure process, which is therefore the heat-addition process of the cycle; the constant-volume blowdown of the exhaust gases becomes a constant specific-volume process, which is therefore the heat-rejection process for the cycle. The  $Ts$  diagram (Fig. 13-9) is constructed for the same processes:

- 1 Isentropic compression  $ab$ ,
- 2 Constant-pressure addition of heat  $bc$ ,
- 3 Isentropic expansion  $cd$ ,
- 4 Constant-volume rejection of heat  $da$

For this cycle

$$Q_{A_{\text{rev}}} = c_p(T_c - T_b)$$

$$Q_{R_{\text{rev}}} = c_v(T_a - T_d)$$

$$\eta_t = \frac{Q_A + Q_R}{Q_A} = 1 - \left(\frac{1}{k}\right) \left(\frac{T_d - T_a}{T_c - T_b}\right)$$

The equation can be changed in form by noting that

$$T_d = \frac{p_d v_d}{p_a v_a} T_a = \frac{p_d}{p_a} T_a$$

$$T_c = \frac{p_c v_c}{p_b v_b} T_b = \frac{v_c}{v_b} T_b$$

and

$$\eta_i = 1 - \frac{1}{k} \left( \frac{T_a}{T_b} \right) \frac{(p_d/p_a) - 1}{(v_c/v_b) - 1}$$

Also,

$$p_d = \left( \frac{v_c}{v_d} \right)^k p_c \quad p_a = \left( \frac{v_b}{v_a} \right)^k p_b$$

Hence,

$$\frac{p_d}{p_a} = \left( \frac{v_c v_a}{v_d v_b} \right)^k = \left( \frac{v_c}{v_b} \right)^k$$

and

$$\eta_i = 1 - \frac{1}{k} \left( \frac{T_a}{T_b} \right) \frac{(v_c/v_b)^k - 1}{(v_c/v_b) - 1}$$

On substituting

$$\frac{T_a}{T_b} = \left( \frac{v_b}{v_a} \right)^{k-1} = \frac{1}{r_1^{k-1}}$$

and calling  $\frac{v_c}{v_b} = L$  the *load ratio*,

$$\eta_i = 1 - \frac{1}{r_1^{k-1}} \left[ \frac{L^k - 1}{k(L - 1)} \right] \quad (13-6)$$

The thermal efficiency of the air-standard Diesel cycle depends on the *compression ratio*  $r_v$ , the *heat-capacity ratio*  $k$ , and the *load ratio*  $L$ . Note that Eqs (13-5) and

(13-6) differ only by the bracketed term, which is always greater than unity, therefore, the efficiency of the Diesel cycle is less than the efficiency of an Otto cycle when comparison is made at the same compression ratio

The results of the Goodenough-Baker analysis for the Diesel cycle are shown in Fig 13-10

**13-10. The Dual (Combination) Cycle.** In the modern CI engine the pressure is not constant during the combustion process but varies

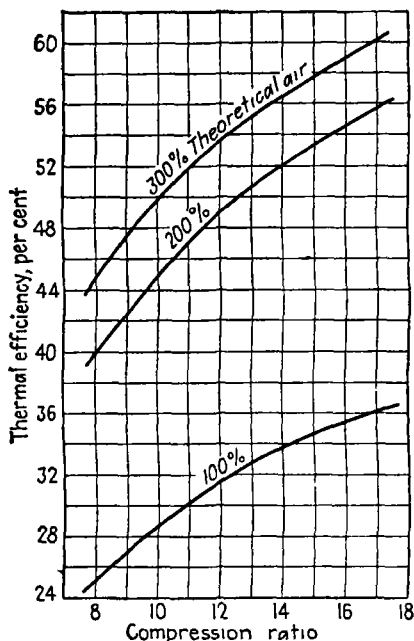


FIG 13-10 Effects of compression ratio and mixture strength upon thermal efficiency of the Diesel cycle (from reference 2)

in the manner illustrated in Fig. 13-8b. A hypothetical cycle with the following processes can be premised for this engine (Fig 13-11)

1. Isentropic compression  $ab$ ,
2. Constant-volume addition of heat  $bb'$ ,
3. Constant-pressure addition of heat  $b'c$ ,
4. Isentropic expansion  $cd$ ,
5. Constant-volume rejection of heat  $da$ .

Discussion of this cycle will be found in Art 13-11:

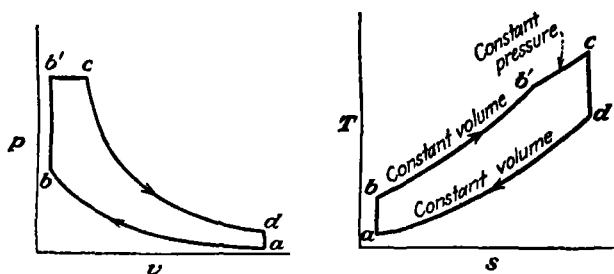


FIG 13-11 Air standard dual cycle

**13-11. Comparison of Air-standard Cycles.** For any given compression ratio and given heat input, the thermal efficiency is highest for the Otto cycle and decreases in the following order

1. Otto cycle,
2. Dual cycle,
3. Diesel cycle

The Otto cycle allows the most complete expansion and attains the highest efficiency because all the heat is added before the expansion process is under way. The Diesel cycle is the worst in this respect since the last portion of the heat is supplied to fluid that has a relatively short expansion before rejection occurs.

On the basis of the same heat input and same maximum pressure, the order of efficiency is

1. Diesel cycle,
2. Dual cycle,
3. Otto cycle

This comparison is important because the real diesel engine can use higher compression ratios than those found in spark-ignition engines.

**Constant Compression Ratio and Heat Input** Figure 13-12 has been constructed for the three theoretical cycles at the same compression ratio and with the same amount of heat supplied. The Otto cycle is shown as  $abcd$ , the dual cycle as

$abb'c'd'$ ; and the Diesel cycle as  $abc''d''$ . All cycles start at the same initial temperature, pressure, and volume at point  $a$ , with isentropic compression to  $b$ . Heat is added under varying conditions for the different cycles. To fulfill the premise of equal heat supplied, the  $Ts$  areas  $fbce$ ,  $fbce''$ , and  $fb b'c'e'$  must be equal. Since

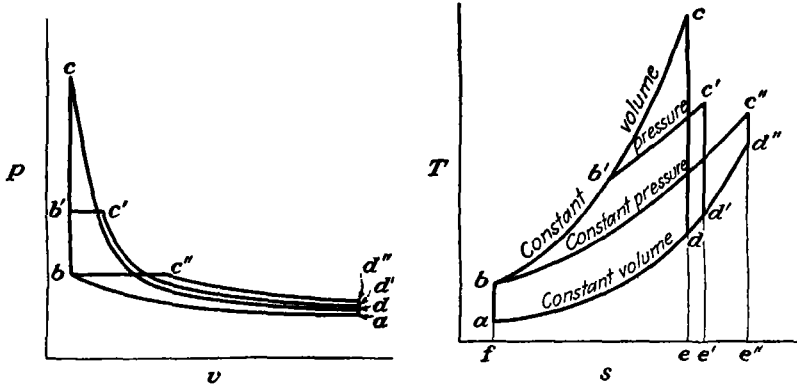


FIG. 13-12 Comparison of theoretical cycles at the same compression ratio and with the same heat input

constant-volume lines are steeper on the  $Ts$  diagram than constant-pressure lines, construction of equal areas for the heat supplied shows point  $c''$  to lie at the point of greatest entropy. With isentropic expansion to the constant-volume line  $ad''$ , the rejected heat for each cycle is shown as the appropriate area under line  $ad''$ . Since the same amount of heat was supplied to each cycle, that cycle will be the

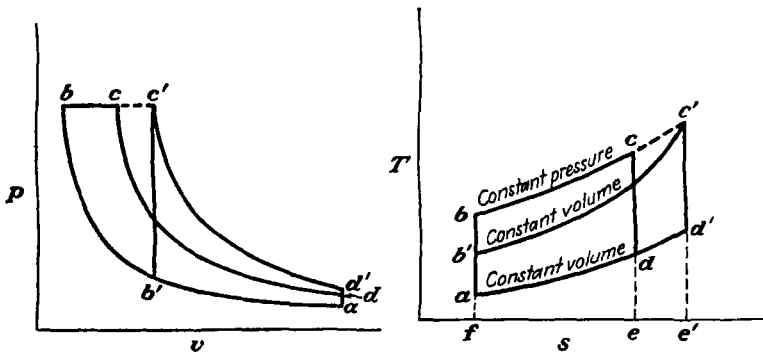


FIG. 13-13 Comparison of Otto and Diesel cycles with same maximum pressure and same heat input

most efficient which rejects the least amount of heat after expansion. This cycle is the Otto with the rejected heat shown as area  $fade$ . The order of efficiencies for the three cycles is as predicted at the beginning of this article.

It is well to emphasize that the considerations just discussed are purely theoretical. The actual CI engine is operated at a high compression ratio, which the

SI engine cannot approach because of the limitations imposed by the detonation characteristics of the fuel-air charge

*Constant Maximum Pressure and Heat Input* Since pressure is often the limiting factor in engine design, the cycles will be compared on the basis of the same maximum pressure and the same heat supplied. Considering only the Otto and Diesel cycles, Fig. 13-13 has been constructed. To fulfill the given conditions, points  $c$  and  $c'$  must lie on a constant-pressure line while the  $Ts$  areas  $fbce$  and  $fb'c'e'$  must be equal. For these conditions the Diesel cycle is the more efficient because less heat is rejected (area  $fadc$  compared with area  $fad'e'$ ). Note that, to achieve this supremacy, the Diesel cycle must operate at a higher compression ratio than the Otto (but this is the usual condition for the practical engine). Similar reasoning would show that the performance of the dual cycle will fall between the two others.

**13-12. Other Definitions and Topics.** The work done by an internal-combustion engine depends on the amount of energy released when a mixture of air and fuel burns. But the air occupies a much greater volume than the fuel, and the induction of the air into the cylinder presents some difficulties. If the engine does not induct the largest possible amount of air, the work output of the engine will be restricted, no matter how much fuel is added. Therefore, a basic requirement for a high-output engine is its capacity for inducting a large amount of air per unit of piston displacement. The efficiency of the induction process is called the *volumetric efficiency* although it is defined as a mass ratio

$$\eta_v = \frac{m}{m_D} \quad (8-25)$$

where  $m$  = mass of air inducted per intake stroke

$m_D$  = mass of air that would fill the displacement volume under atmospheric conditions of temperature and pressure

The volumetric efficiency of the engine may be increased by *supercharging*, a *supercharger* being merely an air compressor that supplies air to the engine. By using a supercharger, a greater mass of air can be packed into the cylinder, and therefore more work can be obtained from the engine. The gain is not proportional to the increase in mass of air supplied to the engine because a considerable portion of the gain must be used to drive the supercharger.

The *brake or shaft work* of the engine is less than the *indicated work*<sup>1</sup> because of the presence of mechanical friction in the engine mechanism. The *mechanical efficiency* of the engine is defined

$$\eta_m = \frac{\text{brake work output}}{\text{indicated work output}} \quad (13-7)$$

<sup>1</sup> See Art. 4-5

Even though an engine has a low mep, or a low volumetric efficiency, or a low mechanical efficiency, the power obtained from the engine may be relatively high, if high cyclic speeds are possible, because power is the time rate of doing work. Modern internal-combustion engines are usually operated, not at the speed of maximum mep (for example), but, rather, at higher speeds where the mep is lower because of mechanical or fluid friction. More power can be obtained because, although the work per cycle is decreased, the number of cycles per second is increased in a greater ratio.

The speed of the engine is given in revolutions per minute (rpm) of the crankshaft. The piston must be stopped and reversed in direction, twice in each revolution of the crank, and the attendant accelerations and decelerations of the reciprocating mass create an inertia force. Since inertia forces are dependent on speed and mass, small engines with light pistons can be operated at higher rpm than large engines. The *mean piston speed* is often specified

$$\text{Mean piston speed} = \text{rpm} \times 2 \times \text{length of stroke} \quad (13-8)$$

When speed or size is limited by design stresses, additional power can be obtained by a *two-stroke* system, which produces a power stroke in every revolution of the crank. Here the exhaust and intake strokes are eliminated by using a *blower* or *scavenging* pump. When the exhaust valve opens near the end of the power stroke, the high-pressure products escape to the atmosphere, air is then blown into the cylinder by the blower to complete the scavenging and also to charge the cylinder. The piston then returns on the second stroke of the cycle, the compression stroke.

The power of the internal-combustion engine depends on the mass rate of air flow into the engine, and this factor in turn is controlled by the size and number of cylinders, the cyclic speed (rpm), and the degree of supercharge. To develop high power output, two methods are available: large engines operated at low rpm (this is CI practice), and small engines operated at high rpm (this is SI practice) either with or without supercharging. In any case the size or complexity of the engine does not lend itself to the production of power in units above 10,000 kw, and smaller units are preferable.

**13-13. Regenerative Cycles.** The thermal efficiency of some cycles can be raised by *regeneration*. Consider Fig 13-14. Here heat is added to the fluid in the constant-volume process *bc* and in the isothermal process *cd*. Heat is rejected from the fluid in the constant-volume process *da* and in the isothermal process *ab*. Note that the



temperature of initial heat rejection is  $T_d$  and the temperature of initial heat addition is  $T_b$ . Because  $T_b$  is less than  $T_d$ , it should be possible to find means for transferring a part of the rejected heat to the heat-addition process. When such means are found, less heat need be supplied from an external source, although the work of the cycle is

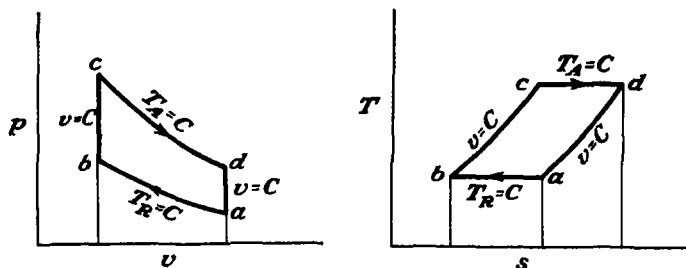


FIG 13-14 Stirling cycle

unchanged and therefore the thermal efficiency of the cycle will be increased; the cycle is now a *regenerative* cycle

The first regenerative cycle was proposed by Robert Stirling in 1827. Stirling's engine is shown in Fig 13-15 and consists of the work piston *A*, the displacer piston *B*, the regenerator *C*, the refrigerator *D*, and the heating chamber *E*. The regenerator is circular and consists of many thin metal plates. The cycle of the Stirling engine is as follows. Piston *B* is at its highest position while piston *A* is at its lowest travel, heat is transferred from the fire to the air in *E*, and the expansion drives the work piston *A* upward (isothermal process *cd* in Fig 13-14). The displacer piston *B* is then lowered, forcing the air in *E* to pass to chamber *F* through the regenerator *C* (constant-volume cooling process *da* in Fig 13-14). The temperature of the regenerator *C* is raised in this process. After *B* has reached the lowest position, piston *A* is brought down, compressing the air in *F*, which is cooled by the refrigerator *D* (isothermal process *ab* in Fig 13-14). The displacer piston *B* is then lifted, forcing the cool air in *F* to return to chamber *E* through the hot regenerator *C* (constant-volume heating process *bc* in Fig. 13-14). The regenerator is cooled in this process, and the cycle is completed.

The Stirling air cycle, while commercially used in a number of engines, was never a complete success because the cycle was limited to low speeds by the slow transfer of heat in external heating.

If the Stirling cycle could be reversibly operated, the efficiency would be equal to that of a Carnot cycle that encountered the same

temperature limits. It is difficult to visualize the engine of Fig. 13-15 being reversibly operated, but the cycle of Fig. 13-14 can be imaginarily treated to attain reversibility. Thus, if the heat capacity of the gas during process  $da$  were the same at each temperature level as in process  $bc$ , the two constant-volume lines on the  $Ts$  diagram would be parallel, and the areas under these lines would be equal. A perfect heat reservoir (or an infinite number of heat reservoirs) could be used to store

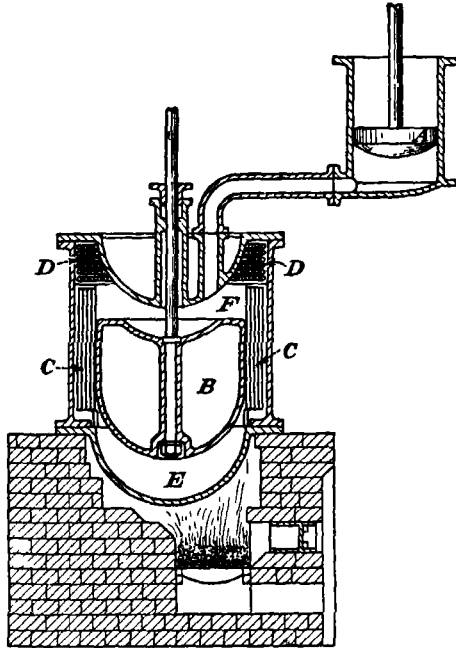


FIG 13-15 First Stirling engine

the thermal energy rejected in process  $da$  and later return the same thermal energy to the working fluid during process  $bc$ . Heat would be added to the cycle from an external source only during process  $cd$ , and heat would be rejected to the surroundings only during process  $ab$ . By the reasoning of Art 5-3, the thermal efficiency of this reversible cycle, which operates between fixed and definite temperature limits, is equal to the Carnot efficiency

$$\eta_t = \frac{T_A - T_R}{T_A}$$

One other regenerative cycle is of historical importance, the Ericsson cycle shown in Fig 13-16. Here perfect regeneration can theoretically

be obtained because the constant-pressure lines  $bc$  and  $da$  are parallel on the  $Ts$  diagram (at least for perfect gases, even if they were not, regeneration is still feasible although reversibility is impossible)

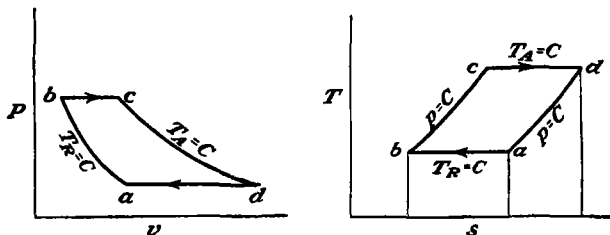


FIG 13-16 Ericsson cycle

**13-14. The Gas Turbine.** The internal-combustion engine is a compact power plant, but it suffers from the limitation of a low mass flow rate. This limitation can be removed by substituting continuous-flow machines for the reciprocating-piston engine while retaining the desirable feature of internal combustion of a fuel with the working fluid. Unfortunately, the flow compression process cannot be as efficiently conducted as nonflow compression. The usual<sup>1</sup> flow compres-

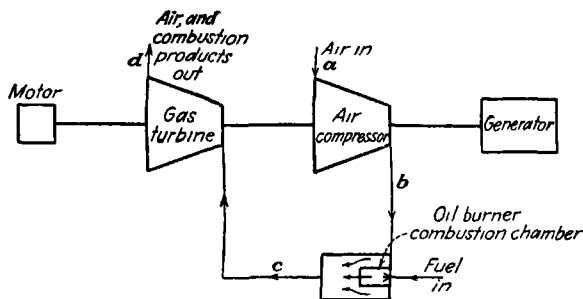


FIG 13-17 Elements of a continuous-combustion gas turbine system

sor first induces a high velocity in the fluid and then transforms the kinetic energy into pressure energy by means of a diffuser or diverging passageway; this is a difficult process to accomplish efficiently. On the other hand, a turbine can be used for the expansion process, and here the fluid can expand to the pressure of the atmosphere and thus attain an expansion ratio that cannot be readily approached by a reciprocating-piston engine. One other disadvantage is inherent in the flow process: the maximum temperature in the reciprocating-piston engine can be high because the process is intermittent, the maximum

<sup>1</sup> See Art 3-6c

temperature in the continuous-flow machine must be relatively low because this temperature is constant in some part of the apparatus.

The basic elements of the continuous-combustion gas-turbine system are illustrated in Fig. 13-17. In this illustration is shown a compressor that compresses the air and forces it into and around the combustion chamber. Only a portion of the air is mixed with the fuel and burned at constant pressure. The high temperature of combustion is reduced by the main body of air passing around the combustion chamber and mixing with the burned products. This mixture, at a temperature of about 1200 F, enters the turbine, which drives both the air compressor and a generator that absorbs the net power. (The small electric motor is used only for starting purposes.)

A speed governor regulates the fuel supply and thereby the turbine inlet temperature. The inlet temperature is restricted by metallurgical problems; for long life, a temperature of 1000 or 1200 F is usually recommended. Experimental work in testing full-scale turbine units and in developing high-temperature materials seems to predict that turbine inlet temperatures of 1500 F or better may be achieved in the near future. With these high temperatures, the gas turbine can compete for the high thermal efficiencies now developed by the CI engine. Even with lower inlet temperatures, the efficiency of the gas turbine may be acceptable for uses where simplicity and high mass flow rates are desirable, or in arid regions because a water supply is unnecessary. In general, fuels for the gas turbine can be cheaper than the fuels for internal-combustion engines because detonation is not a factor; experiments also indicate that powdered coal may prove successful.

**13-15. The Brayton (Joule) Cycle.** The gas-turbine process for analysis can be considered to be a cycle as represented in Fig. 13-18. The diagrams in Fig. 13-18 are constructed for the following idealized processes

- 1 Isentropic compression  $ab$ ,
- 2 Constant-pressure addition of heat  $bc$ ,
- 3 Isentropic expansion  $cd$ ,
- 4 Constant-pressure rejection of heat  $da$ .

The working fluid throughout the cycle is considered to be of constant composition. (This assumption does not seriously weaken the analysis because the amount of fuel burned in the real cycle has small effect on the heat capacities of the fluid.) The thermal efficiency of the cycle is

$$\eta_t = \frac{Q_A + Q_R}{Q_A} = \frac{c_p(T_c - T_b) - c_p(T_d - T_a)}{c_p(T_c - T_b)}$$

$$\eta_t = 1 - \frac{T_d - T_a}{T_c - T_b}$$

By the same procedure as in Art 13-7 it can be shown that

$$\eta_t = 1 - \left(\frac{v_b}{v_a}\right)^{k-1} = 1 - \frac{1}{r_p^{k-1}} \quad (13-5)$$

Thus, the thermal efficiency of the Brayton cycle is equal to that of the Otto cycle for the same compression ratio. But the pressure ratio

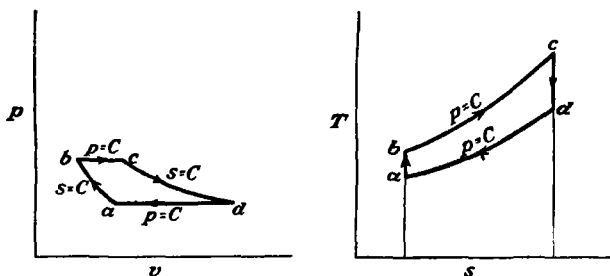


FIG 13-18 Brayton (Joule) cycle

[Eq (13-3)] is more often used as the parameter for expressing gas-turbine efficiencies, and Eq (13-5) in terms of this ratio is

$$\eta_t = 1 - \left(\frac{p_a}{p_b}\right)^{\frac{k-1}{k}} = 1 - \frac{1}{r_p^{\frac{k-1}{k}}} \quad (13-9)$$

Note that the thermal efficiency of the Brayton cycle, like that of the Otto cycle, depends on the pressure ratio and on the heat-capacity relationship for the fluid, and not on the load or the maximum temperature

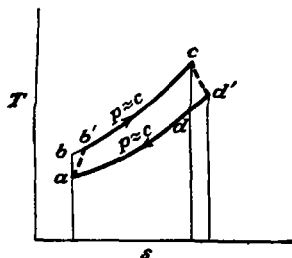


FIG 13-19 Irreversible gas turbine cycle

Since the real processes for the gas turbine are irreversible, the cycle pictured in Fig 13-19 is more representative. For this irreversible cycle

$$\eta_t = \frac{\Sigma W}{Q_A} = \frac{W_t + W_c}{Q_A}$$

The turbine work can be expressed in terms of the isentropic work and the expansion (engine) efficiency (Art 12-1)

$$W_t = (h_c - h_{d'}) = (h_c - h_d)\eta_e$$

The compression work can be similarly expressed:

$$W_c = (h_a - h_{b'}) = (h_a - h_b) \frac{1}{\eta_c}$$

The heat added is

$$Q_A = h_c - h_{b'}$$

And the thermal efficiency is

$$\eta_t = \frac{(h_c - h_d)\eta_c - (h_b - h_a)(1/\eta_c)}{h_c - h_{b'}} \quad (13-10)$$

This equation can be rearranged, for perfect gases, to eliminate the properties at states  $d$ ,  $b$ , and  $b'$  by noting that

$$\Delta h = c_p \Delta t$$

$$\eta_c = \frac{h_b - h_a}{h_{b'} - h_a} = \frac{T_b - T_a}{T_{b'} - T_a}$$

and by defining  $x$  as

$$x = \frac{T_b}{T_a} = \frac{T_c}{T_d} = r_p^{\frac{k-1}{k}}$$

Then,

$$T_{b'} = T_a \left( \frac{x-1}{\eta_c} + 1 \right)$$

With these equations

$$\eta_t = \frac{T_c \left( 1 - \frac{T_d}{T_c} \right) \eta_c - \frac{T_a}{\eta_c} \left( \frac{T_b}{T_a} - 1 \right)}{T_c - T_a \left( \frac{x-1}{\eta_c} + 1 \right)}$$

$$\eta_t = \frac{T_c \left( 1 - \frac{1}{x} \right) \eta_c - \frac{T_a}{\eta_c} (x-1)}{T_c - T_a \left( \frac{x-1}{\eta_c} + 1 \right)}$$

$$\eta_t = \frac{\left( \frac{T_c \eta_c}{x} - \frac{T_a}{\eta_c} \right) (x-1)}{T_c - T_a \left( \frac{x-1}{\eta_c} + 1 \right)} \quad (13-11)$$

Equation (13-11) when plotted, as thermal efficiency against pressure ratio for various maximum temperatures ( $T_c$ ), yields Fig 13-20. This figure shows that an optimum compression ratio exists for each turbine inlet temperature. Note that increasing the temperature

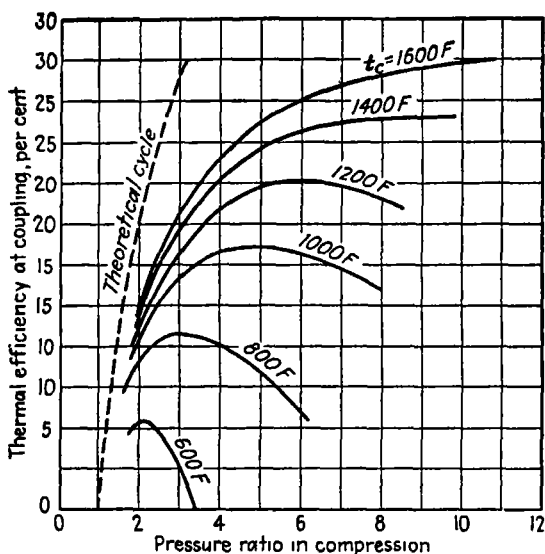


FIG 13-20 Effects of compression ratio and turbine inlet temperature on the thermal efficiency of the nonregenerative Brayton cycle (from reference 3) ( $t_c$  = turbine inlet temperature,  $\eta_e = \eta_c = 0.85$ ,  $t_a = 60$  F)

from 800 to 1600 F more than doubles the optimum thermal efficiency

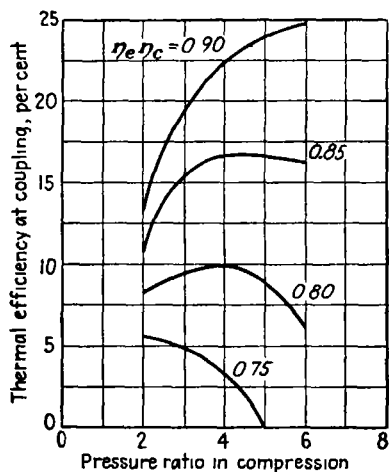


FIG 13-21 Effects of compression ratio and turbine-compressor efficiencies on the thermal efficiency of the nonregenerative Brayton cycle (from reference 3) ( $\eta_e$  turbine efficiency,  $\eta_c$  compressor efficiency,  $t_c = 1000$  F,  $t_a = 60$  F)

Reducing the inlet temperature, as a means of reducing the output, causes a serious drop in efficiency if the pressure ratio remains constant (The pressure ratio will remain essentially constant when the turbine compressor unit operates at constant speed)

When the inlet temperature  $T_c$  is held constant while the compression and expansion efficiencies are varied, Eq (13-11) yields Fig 13-21. Here it is seen that the process efficiencies also determine the optimum compression ratio.

**Example 3:** Air at 14.7 psia and 60 F is compressed to 54 psia and a final temperature of 340 F. Fuel is then burned in amount to increase the temperature to 1000 F before the gas enters the tur-

bine If the exhaust from the turbine is at 640 F and heat losses are considered to be zero, what will be the thermal efficiency of the unit?

**Solution:** The amount of fuel burned is small, and the chemical composition of the mixture can be considered as not appreciably different from that of air Table X (Appendix) will be used for finding the enthalpy of the air at each state (lettering following that of Fig 13-19)

$$h = u + pv$$

$$\text{At 60 F or 520 R} \quad h_a = 0 + 1033 = 1033 \text{ Btu/mole air}$$

$$\text{At 340 F or 800 R} \quad h_{b'} = 1403 + 1589 = 2992 \text{ Btu/mole air}$$

$$\text{At 1000 F or 1460 R} \quad h_c = 7823 \text{ Btu/mole air}$$

$$\text{At 640 F or 1100 R} \quad h_{d'} = 5142 \text{ Btu/mole air}$$

$$\text{Work from turbine } (h_c - h_{d'}) = 2681 \text{ Btu/mole air}$$

$$\text{Work to compressor } (h_a - h_{b'}) = -1959 \text{ Btu/mole air}$$

$$\text{Net work} = 722 \text{ Btu/mole air}$$

$$\text{Heat supplied } (h_c - h_{b'}) = 4831 \text{ Btu/mole air}$$

$$\eta = \frac{\Sigma W}{Q_A} = \frac{(722)(100)}{4831} = 15 \text{ per cent} \quad \text{Ans}$$

The mass of fuel, which was neglected in the above calculation, can be computed Assume that the fuel is decane with a lower heating value of 2,733,000 Btu/mole (Table XII, Appendix) Then, the moles of fuel burned per mole of air are

$$\frac{Q_A \text{ Btu/mole air}}{\Delta H \text{ Btu/mole fuel}} = \frac{4831}{2,733,000} = 0.00176 \frac{\text{moles fuel}}{\text{moles air}}$$

The mass ratio, in pounds, is

$$\frac{0.00176(142)}{29} = 0.00862 \frac{\text{lb}_m \text{ fuel}}{\text{lb}_m \text{ air}}$$

This is an air-fuel ratio of

$$AF = \frac{1}{0.00862} = 116 \frac{\text{lb}_m \text{ air}}{\text{lb}_m \text{ fuel}}$$

**13-16. The Regenerative Gas-turbine Cycle.** Inspection of Fig 13-19 reveals that the temperature of the exhaust gases at state  $d'$  is higher than the temperature of the compressed air at state  $b'$ , and, because of this, the gas-turbine cycle can be regenerated The regeneration is accomplished by installing a heat exchanger in the flow system as illustrated in Fig 13-22 Here the compressed air is passed through a bundle of tubes or flat plates while the hot exhaust gas is circulated between the tubes or plates In this manner the air is increased in temperature before reaching the combustion chamber, and thus less fuel need be burned to attain a specified turbine inlet temperature. The heat exchanger must be carefully designed, an excessive pressure drop of either the air or exhaust gas may nullify the anticipated gain in efficiency Note that lowering the compression



ratio increases the temperature difference available for regeneration, and, at high compression ratios, regeneration becomes impossible

The theoretical gain in thermal efficiency can be calculated for various degrees of *efficiency* of the regenerator. The *efficiency* is defined (letters correspond to Fig 13-22)

$$\eta_r = \frac{\text{actual temperature rise}}{\text{maximum temperature rise}} = \frac{t_y - t_{b'}}{t_{d'} - t_{b'}} \quad (13-12)$$

If the regenerator had infinite surface,  $t_y$  and  $t_{d'}$  would be equal. The size of the practical regenerator allows an  $\eta_r$  of 0.50 to 0.75 without excessive pressure drop. The thermal efficiency of the regenerative

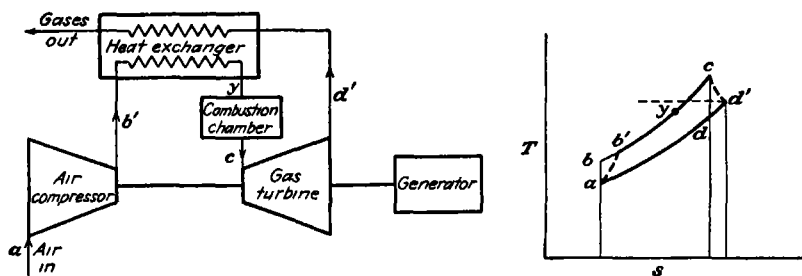


FIG 13-22 Regenerative gas turbine system

cycle of Fig 13-22 is given by Eq (13-11) when the term in the denominator involving  $T_a$  is replaced by  $T_y$

$$\eta_t = \frac{\left( \frac{T_c \eta_c}{x} - \frac{T_a}{\eta_c} \right) (x - 1)}{T_c - T_y}$$

The temperature  $T_y$  is found by Eq (13-12).

$$T_y = \eta_r (T_{d'} - T_{b'}) + T_{b'}$$

and  $T_{b'}$  can be expressed in terms of  $T_b$ ,  $T_a$ , and  $\eta_c$ , while  $T_{d'}$  is expressed in terms of  $T_c$ ,  $T_d$ , and  $\eta_e$ . With these substitutions

$$T_y = T_a \left( \frac{x-1}{\eta_c} + 1 \right) (1 - \eta_r) + (\eta_r T_c) \left[ 1 - \eta_e \left( \frac{x-1}{x} \right) \right]$$

The thermal efficiency then equals

$$\eta_t = \frac{\left( \frac{T_c \eta_c}{x} - \frac{T_a}{\eta_c} \right) (x - 1)}{T_c - \left\{ T_a \left( \frac{x-1}{\eta_c} + 1 \right) (1 - \eta_r) + (\eta_r T_c) \left[ 1 - \eta_e \left( \frac{x-1}{x} \right) \right] \right\}} \quad (13-13a)$$

This equation, although formidable in appearance, is quite easily solved. For cases where  $\eta_r = 1.0$

$$\eta_t = 1 - \frac{T_a x}{T_c \eta_c \eta_o} \quad (13-13b)$$

And when  $\eta_o = \eta_c = 1.0$

$$\eta_t = \frac{(T_c - T_a x)(x - 1)}{T_c(x - \eta_r) - T_a x^2(1 - \eta_r)} \quad (13-13c)$$

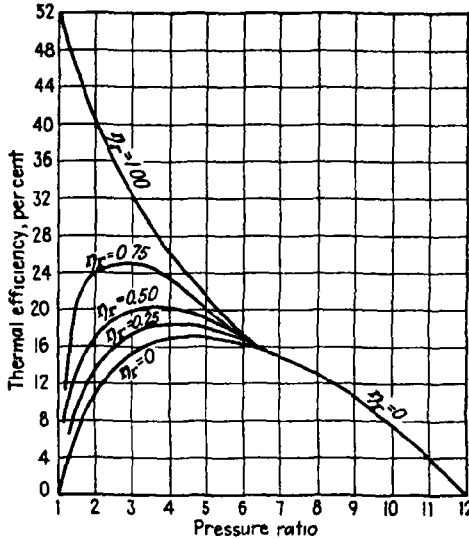


FIG 13-23 Effects of compression ratio and degree of regeneration on the thermal efficiency of a gas turbine cycle ( $\eta_o = \eta_c = 0.85$ ,  $t_a = 1000$  F,  $t_a = 60$  F)

Equation (13-13a) when plotted as thermal efficiency versus pressure ratio for various degrees of regeneration yields Fig 13-23<sup>1</sup>. Note that regeneration decreases the pressure ratio for optimum efficiency.

**13-17. Other Improvements in the Gas-turbine Cycle.** The work ratio of the gas-turbine cycle can be raised if the isentropic compression process is replaced by isothermal compression. Figure 13-24 shows that this substitution increases the net work of the cycle (area  $abcd$  is larger than area  $ab'cd$ ) and decreases the thermal efficiency (heat added from  $b$  to  $b'$  is less effective than heat added from  $b'$  to  $c$  because a greater percentage is rejected). The decrease in thermal efficiency is more than removed when the cycle is regenerated because the energy

<sup>1</sup> The heat exchanger must be discarded at high compression ratios, or regeneration may become negative, that is, the exhaust gases will be increased in temperature

available in the exhaust gases (area under  $ad$ ) is sufficient to raise the temperature from  $T_b$  to the limiting temperature  $T_d$ . Since isothermal compression is not a practical flow process, the real system employs intercooling and regeneration as shown in Fig 13-25

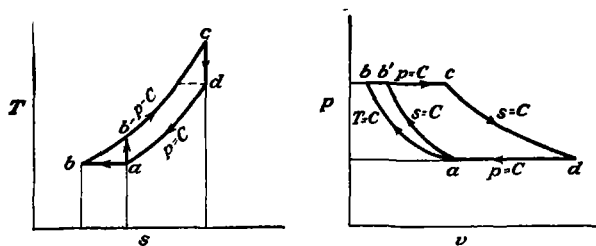


FIG 13-24 The gas turbine cycle with isothermal and isentropic compression

The work ratio of the cycle can also be raised by injecting water into or around the combustion chamber. This procedure does not affect the work of the compressor, but the steam that is formed from vaporizing the water increases the mass flow to the turbine, lowers the  $k$  value of the mixture entering the turbine, and therefore increases<sup>1</sup>

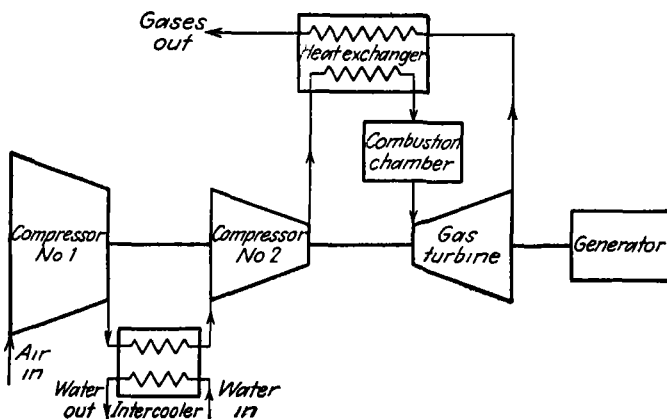


FIG 13-25 Gas turbine system with intercooling and regeneration.

the work output (The work spent in pumping the water is negligible) This practice, of course, reduces the thermal efficiency because more fuel must be burned to raise the temperature and supply the latent heat of vaporization of the water. The water can also be injected into the air stream before compression or into the compressed air at a location preceding the regenerator; apparently, this last location is a

<sup>1</sup> See Art 8-9a and Eq (8-13)

patent claim<sup>1</sup> by Lysholm Note that water injected at any location that precedes the regenerator will probably result in a gain in thermal efficiency unless the energy available in the exhaust gases is insufficient to vaporize the water

The work ratio of the cycle can also be increased by reheating the air, after partial expansion in one turbine, before the air is admitted to a final turbine (Fig 13-26) In this instance the thermal efficiency

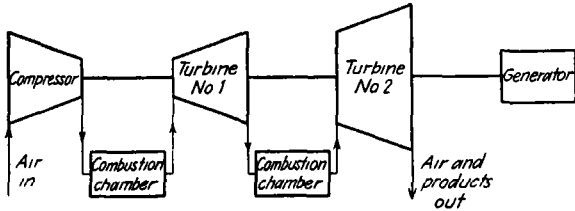


FIG 13-26 Gas turbine system with reheat

of the real system will probably be increased by the reheat because the work of the compressor, which affects the thermal efficiency, is not changed

Improvement in part-load efficiency can be obtained by using two turbines as shown in Fig 13-27; one turbine drives the compressor

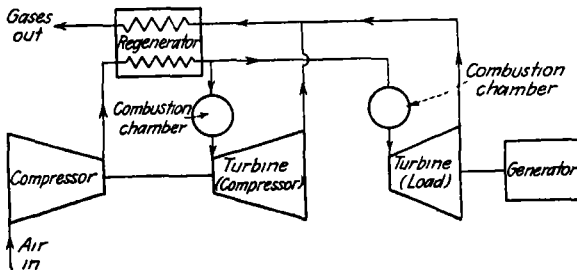


FIG 13-27 Dual turbine system

alone while the second turbine drives the load A separate combustion chamber can be used for each turbine With this arrangement, the turbine driving the compressor can always be operated at the best speed for the compressor while the inlet temperature is maintained at the design value Fractional loads are secured by varying the inlet temperature to the load turbine, which can be operated at variable speed as dictated by the load requirements Here the inefficiency of low temperature or low speed is confined to only a portion of the entire system

<sup>1</sup> See reference 4

**13-18. Closed and Semiclosed Systems.** The open gas-turbine system is independent of a cooling source since it rejects hot waste

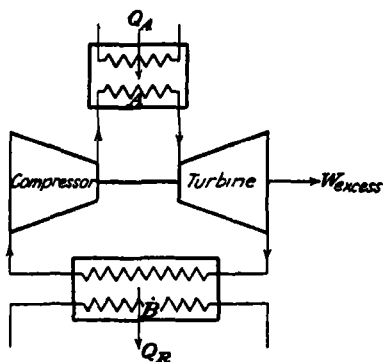


FIG 13-28 Closed system gas turbine cycle.

gases to the atmosphere; this factor and the simplicity of the system have been major reasons for promoting development. A *closed system*, on the other hand, continuously circulates the same fluid and requires heat exchangers for the heat-addition and -rejection processes. Figure 13-28 depicts such a cycle. Combustion of the fuel takes place in the air heater *A* and not internally within the system, while water is used to cool the gases in the heat exchanger *B*. The advantages of the closed system are as follows.

- 1 Higher pressures can be used throughout the cycle, and therefore higher densities of the working fluid are obtained. This allows all parts of the system to be made smaller, smaller physical dimensions allow higher temperatures for a given stress limit.
- 2 The working fluid is clean, not contaminated with products of combustion; deposits on the turbine or compressor blades and wear or erosion of the turbine and compressor are reduced.
- 3 The working fluid can be a monatomic gas that has a more favorable heat-capacity ratio ( $k$ ) than air.
- 4 Thermal efficiency at part load is high because part load can be secured by varying the density of the working fluid without varying the temperature. (Of course, a control system must be added to Fig 13-28 if the density of the fluid is to be changed by adding or subtracting working fluid.)
- 5 A cheap fuel, such as coal, can be used.

Accompanying these advantages are the following disadvantages

1. The efficiency of internal combustion has been eliminated by substituting a heat exchanger and an external furnace.
2. A coolant must be available.
3. Complexity and cost of the system have been increased.

*Semiclosed* systems have been proposed to secure advantages 1 and

4 of the closed cycle. In Fig. 13-29 is shown a Swiss design. The main and high-pressure circuit for the fluid contains turbine  $T_2$  and compressor  $C_2$ ; the control circuit contains turbine  $T_1$  and compressor  $C_1$ . Air is bled from the main circuit at  $A$  to support combustion of

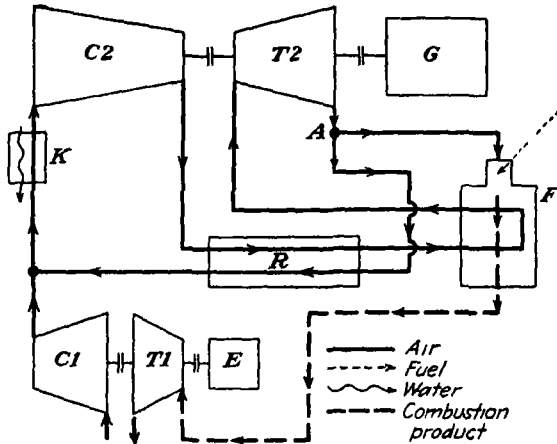


FIG 13-29 Sulzer Bros semiclosed gas turbine system (from reference 4)

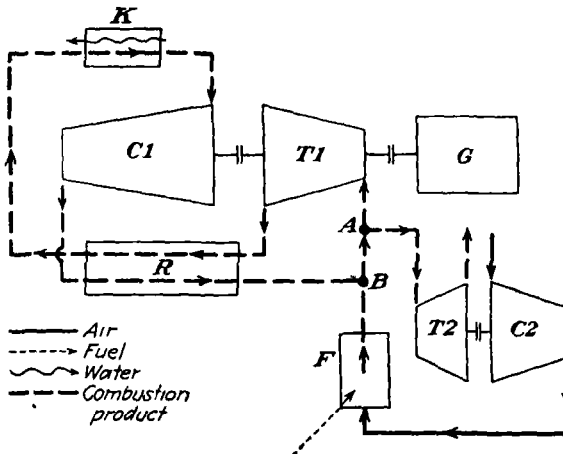


FIG. 13-30. Westinghouse semiclosed gas turbine system (from reference 4)

the fuel that is introduced in the furnace  $F$ . The products of combustion, which are at a pressure greater than atmospheric, are then led to the control turbine  $T_1$  and, finally, exhaust to the atmosphere. Note that turbine  $T_1$  drives a compressor  $C_1$ , which need only supply fresh air to the main circuit to replace the air that was bled for combustion. The electrical machine  $E$  is run either as a generator or as a

motor to balance the output. The system of Fig. 13-29 confines the products of combustion to the control turbine and thus only clean fluid passes through the main circuit.

The Westinghouse semiclosed system is shown in Fig. 13-30. Here the furnace has been eliminated, and the fuel is burned just prior to entering the main air stream. In this system, the products of combustion pass through the main circuit.

**13-19. The Explosion Gas Turbine.** Most development work on gas turbines in this country has included only constant-pressure combustion of the fuel. In Europe, experiments have been made for many years on gas turbines that utilize *constant-volume* combustion although

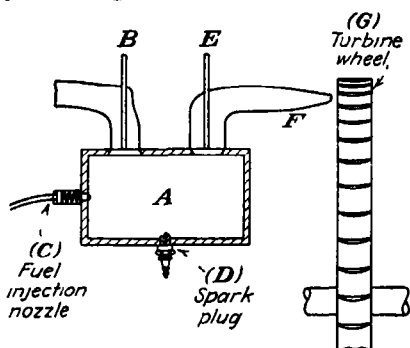


FIG. 13-31 Elements of the explosion gas turbine system

commercial success of such turbines appears to be lacking. The Holzwarth or explosive turbine is graphically illustrated in Fig. 13-31. Air is forced into the combustion chamber *A* from the air compressor through a valve *B*. Fuel is sprayed into this air by injection valve *C*, and the mixture is ignited by the spark plug *D*. The pressure rise opens valve *E*, allowing the gases to flow to the nozzles of the turbine.

Following the expansion, valve *E* is held open (by mechanism not shown), and scavenging air is allowed to enter through valve *B* and pass through the turbine, thus cooling the parts that were subjected to high temperatures. Valve *E* then closes, and the operation is repeated. A number of these combustion chambers are located around the perimeter of the turbine. Along with the complication of the valves and valve gear, note that the flow from the nozzle is intermittent and the fluid velocities are variable. Since nozzle and blade angles are fixed, the best efficiency is obtained at one particular pressure differential across the nozzle.

### Problems

The instructor may also specify

- a Keenan Air Tables for solution
- b Variable heat capacity of air for addition of heat
- c Air Chart for solution (Fig. IX, Appendix)

1. Determine the  $\text{imep}$  for the Carnot cycle of Example 1, Chap. XII (assume system is nonflow)

2. Check the equation in Art. 13-3 for the net work of a Carnot cycle by

substituting the expression for the work of each process in the general equation

$$\Sigma W = W_{ab} + W_{bc} + W_{cd} + W_{da}$$

and reduce

**3** Repeat Example 1 of this chapter, assuming that helium is the working fluid

**4.** An engine operates on an air cycle. Air at 30 psia and 520 R is isentropically compressed to 450 psia. Heat is added at constant pressure until the temperature is 2000 R, and then an isentropic expansion proceeds to 30 psia. Heat is rejected at constant pressure, and the initial state is regained. Find for 1 lb<sub>m</sub> of air (a) the temperature at the end of compression, (b) the heat added at constant pressure, (c) the temperature at the end of expansion, (d) the heat rejected at constant pressure, (e) the volume at each point of the cycle, (f) the entropy change for each process, and plot (g)  $Ts$  and  $pv$  diagrams and (h) the cycle efficiency

**5.** One pound mass of air in a Carnot cycle has a volume of 0.1 cu ft and a pressure of 3,000 psia at the start of the isothermal expansion stroke. If the thermal efficiency is 40 per cent and the isothermal expansion ratio is 10, find heat added and rejected, work done, mep, and the pressure at the end of each process

**6.** A Carnot cycle with air as the fluid has a thermal efficiency of 50 per cent and an isothermal expansion of 2. If 64 Btu of heat are supplied to the cycle, which has a volume of 5 ft<sup>3</sup> and a pressure of 100 psia at the start of isothermal expansion, find the work, mep, and pressure at the end of each process

**7** An Otto cycle using air with constant-volume addition of heat operates at a compression ratio of 6. Heat is supplied of amount 1280 Btu/lb<sub>m</sub> air. At the start of the cycle the temperature is 540 R and the pressure is 14.7 psia. Find the temperatures and pressures at key points of the cycle and the mep

**8.** Find the thermal efficiency and mep for the cycle of Prob 7

**9.** For an Otto cycle with compression ratio of 4 but otherwise with the same data as Prob 7, find the amount of heat rejected

**10.** Plot thermal efficiency for the air-standard Otto cycle against compression ratio for values of the ratio from 1 to 10

**11.** Compute the thermal efficiency of an Otto cycle that has a combustion-chamber volume that is 20 per cent of the piston displacement

**12.** For the data of Prob 7, determine the horsepower if the cycle contains 0.1 lb<sub>m</sub> of air and the speed is 2,000 cycles per min

**13.** Consider the data of Prob 7 to be that of a Diesel cycle with constant-pressure addition of heat. Find the pressures and temperatures at key points of the cycle, the mep, and the thermal efficiency

**14** The compression ratio for a Diesel cycle is 14, the initial pressure is 14.7 psia, and the temperature is 60 F. The temperature at the end of the combustion process is 3000 F. Determine the thermal efficiency of the cycle if air is the fluid

**15** The initial temperature in a Diesel cycle is 14 psia and the temperature is 80 F. The temperature before combustion is 700 F and after combustion it is 3000 F. Determine thermal efficiency of the air-standard cycle

**16.** Compare the Otto, Diesel, and dual cycles on the  $Ts$  and  $pv$  diagrams for conditions of same maximum pressure and temperature. Determine which cycle is the most efficient

**17.** Repeat Prob 16 but for equal outputs from each cycle (compression ratios will differ)



18. At the start of isothermal compression in the Stirling cycle, the pressure is 14.7 psia and the temperature is 540 R while the compression ratio is 8 (same data as in Example 2). Determine the work, mep, and thermal efficiency of the cycle, if non-regenerative, and heat added is 1280 Btu lb<sub>m</sub><sup>-1</sup> air.

19. The maximum pressure in an Ericsson cycle is 600 psia, and the maximum temperature is 1200 F. The minimum pressure is 14.7 psia and minimum temperature is 80 F. Determine the work, mep, thermal efficiency, and compression ratio of the nonregenerative cycle.

20. Repeat Prob. 19 for the Stirling cycle.

21. Repeat Prob. 19 for the Carnot cycle.

22. Repeat Prob. 19 for the Otto cycle.

23. Repeat Prob. 19 for the Diesel cycle.

24. Repeat Prob. 19 for the Brayton cycle.

25. Superimpose the results of Probs. 19 to 24 on the  $Ts$  and  $pv$  diagrams. Table all results to facilitate comparison of cycles.

26. A continuous-combustion turbine system operates with pressure ratio of 3. What will be the ideal thermal efficiency?

27. Repeat Prob. 26, assuming that the compression ratio is 3.

28. The turbine of Prob. 26 has compressor and turbine efficiencies of 85 per cent while the inlet temperature is 1200 F. Calculate the thermal efficiency and work ratio (atmospheric conditions, 14.7 psia and 60 F).

29. Repeat Prob. 28, assuming that a regenerator is added with efficiency of 75 per cent.

30. Repeat Prob. 29, assuming that the regenerator introduces a pressure drop of 2 psia between compressor and turbine (pressure ratio of turbine is now less than 3).

31. What will be the thermal efficiency and work ratio of a gas-turbine system if the inlet air is 100 F and 14.7 psia, the outlet from the compressor is 50 psia and 400 F, and the combustion temperature is 1200 F, falling to 840 F at exhaust?

32. Determine the compression and expansion efficiencies for the data of Prob. 31.

33. A reversible turbine with pressure ratio of 4 has an inlet temperature of 1200 F. Atmospheric conditions are 60 F and 14.7 psia. Determine the thermal efficiency and work ratio for (a) isentropic compression, (b) isothermal compression, (c) two-stage isentropic compression with perfect intercooling.

34. Repeat Prob. 33, assuming that a perfect regenerator is used in each instance. Compare results with those for Prob. 33.

35. Derive Eq. (13-13b) starting from the basic relationship

$$\eta_t = \frac{\sum W}{Q_A}$$

36. Equation (13-13a), when plotted as thermal efficiency versus pressure ratio, will yield curves that cross the curve for zero regeneration (not shown in Fig. 13-23). Explain why this occurs.

37. A gas-turbine system has pressure ratio of 4 and compressor and engine efficiencies of 83 per cent while the maximum temperature is 1300 F. Atmospheric conditions are 60 F and 14.7 psia. Determine the thermal efficiency and work ratio.

38. Water at 60 F is introduced into the combustion chamber of the system

of Prob 37, and the gas temperature of 1700 F is reduced to the same value as before, 1300 F. Assume that the heat of vaporization of the water is  $1000 \text{ Btu lb}_m^{-1}$  and the constant-pressure heat capacity is  $0.5 \text{ Btu lb}_m^{-1} \text{ F}^{-1}$ . Assume, too, that the water-and-air mixture entering the turbine is considered to be only air although the mass flow is increased by the presence of the water. Calculate the work ratio and thermal efficiency for the system.

39. Repeat Prob 38, assuming that a regenerator is present and the same amount of water is introduced before the regenerator, which has infinite surface

### Symbols

$AF$	air to fuel mass ratio
bmeP	brake mean effective pressure
$c$	heat capacity
$C$	constant
$F$	Fahrenheit temperature scale
$H$	enthalpy
$h$	specific enthalpy
imeP	indicated mean effective pressure
$k$	ratio of $c_p$ to $c_v$
$L$	load ratio
$m$	mass, also, mass flow rate
mep	mean effective pressure
$n$	polytropic exponent
$p$	pressure
$Q$	heat
rpm	revolutions per minute
$r_p$	pressure ratio
$r_v$	compression or expansion ratio (volume ratio)
$R$	Rankine temperature scale
$R$	gas constant (universal or specific)
$s$	specific entropy
$t$	Fahrenheit temperature
$T$	absolute temperature
$u$	specific internal energy
$v$	specific volume
$V$	volume
$V_D$	piston displacement (volume)
$W$	work
$x$	isentropic temperature ratio

### Subscripts

$A$	added
$c$	compressor
$D$	displacement
$p$	constant pressure
rev	reversible
$R$	rejected
$T$	constant temperature
$t$	turbine
$v$	constant volume, also, volumetric

## Greek

$\eta_c$	(eta)	compression (compressor) efficiency
$\eta_e$		expansion (engine or turbine) efficiency
$\eta_m$		mechanical efficiency
$\eta_r$		efficiency of regeneration
$\eta_t$		thermal efficiency
$\eta_v$		volumetric efficiency
$\Sigma$	(sigma)	summation

## Suggested References

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- 3 RETTALIATA, J T The Combustion Gas Turbine, *Trans. ASME*, **63** (No 2), 115-123 (February, 1941)
- 4 FERNALD, E Gas Turbine Patents, *Mech Eng*, **58** (No 8), 727-742 (August, 1946)
- 5 SAWYER, R T "The Modern Gas Turbine," Prentice-Hall, Inc, New York, 1945

**CLASS ASSIGNMENTS**



## CHAPTER XIV

### REFRIGERATION

Refrigeration is the production and maintenance in a space of a temperature lower than that of the surroundings, this science is a necessary part of many industrial processes as well as a very desirable part of modern conveniences

**14-1. Definitions.** Not long ago, natural ice was the principal means of refrigeration, and therefore the refrigeration capacity was related to the latent heat of fusion of ice. A *ton of refrigeration* is, closely, the cooling effect or heat exchange equivalent to that obtained by melting 1 ton of ice at 32 F into water at 32 F Or precisely,<sup>1</sup> by arbitrary definition,

$$1 \text{ standard ton refrigeration} = (2,000 \text{ lb}_m) (144 \text{ Btu/lb}_m) \\ = 288,000 \text{ Btu}$$

More often the ton of refrigeration is considered to be a rate

$$1 \text{ standard commercial ton refrigeration} = 288,000 \text{ Btu/24 hr} \\ = 12,000 \text{ Btu/hr} = 200 \text{ Btu/min} \quad (14-1)$$

To obtain the cooling effect called *refrigeration*, work (or available energy) must be expended The *coefficient of performance* is defined as the ratio of the refrigeration to the work supplied <sup>2</sup>

$$\text{cop} = \frac{Q_A}{-W} \quad (14-2)$$

The refrigeration  $Q_A$  is the heat added to the working substance in the cycle, and  $W$  is the work required to drive the apparatus The value of the cop can be less or greater than unity

Another gauge of the performance of the refrigerating machine is the horsepower per ton of refrigeration

$$\text{Hp/ton} = \frac{200}{\text{cop}(42.4)} = \frac{4.71}{\text{cop}} \quad (14-3)$$

<sup>1</sup> The latent heat of fusion of ice at 32 F is 143.35 Btu lb<sub>m</sub><sup>-1</sup>

<sup>2</sup> By the convention used in this text, work supplied to a system is a negative number, thus, the cop defined by Eq (14-2) is a positive number

**14-2. The Carnot Heat Pump.** When the heat-engine cycle is reversed, a refrigeration cycle is obtained. In Fig 14-1, the Carnot heat pump (Art 5-3), employing a mixture of a liquid and its vapor as the working substance or *refrigerant*, is illustrated. Here the cycle consists of the following processes:

- ab* Isentropic expansion to the low temperature  $T_A$
- bc* Heat added in the *evaporator* at the low temperature  $T_A$
- cd* Isentropic compression from the low temperature  $T_A$  to the rejection temperature  $T_R$
- da* Heat rejected in the *condenser* at the temperature  $T_R$

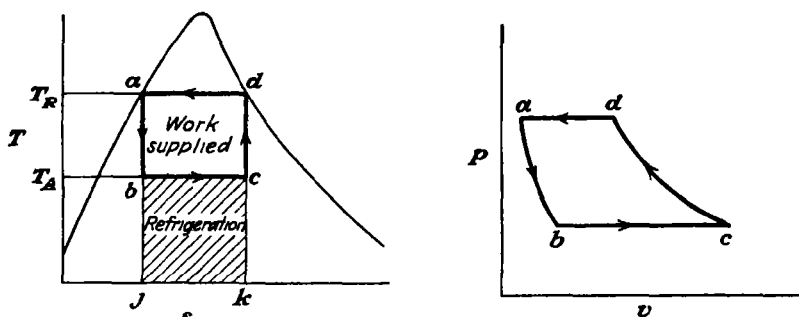


FIG 14-1 The Carnot refrigeration cycle (The refrigerant is a vapor)

The refrigeration is proportional to area  $j b c k$ ; the work supplied is proportional to area  $a b c d$ , and the heat rejected is proportional to area  $j a d k$ . For this cycle,

$$\text{cop}_{\text{Carnot}} = \frac{Q_A}{-W} = \frac{Q_{bc}}{-(Q_{bc} + Q_{da})} = \frac{T_A}{T_R - T_A} \quad (14-4)$$

It has been demonstrated (Art 5-3) that, *between fixed temperature limits*, all reversible engines have the same thermal efficiency, the thermal efficiency of the Carnot cycle. Thus, the work of the Carnot cycle is the maximum work that can be obtained from transformation of heat energy in a heat-engine cycle. But if the Carnot cycle (or any reversible cycle) delivers the maximum work as a heat engine, it must therefore require the least work for the reversed operations as a heat pump. For consider Fig 14-2: if a heat pump could be found that would require less work than a reversed Carnot engine, a system could be devised that would produce work by transforming heat supplied by a low-temperature reservoir. The Second Law denies the existence of such a system. Thus, the coefficient of performance of a reversible

engine is the optimum performance for the refrigeration machine. Moreover, all reversible heat pumps operating between the same temperature limits will have the same coefficient of performance no matter what fluid is used as the refrigerant or what pressures are experienced in the system. Then, the work or power required per ton of refrigeration will also be independent of the refrigerant and dependent only upon the temperatures of source and sink. These conclusions are valid only for the reversible cycle because the irreversibilities and the temperature limits of the real cycle will be affected in greater or less degree by the properties of the refrigerant (Table 14-1).

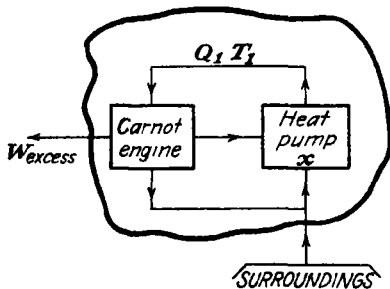


FIG 14-2 A system that would produce work from heat supplied by the atmosphere (assumption heat pump  $x$  requires less work than a reversed Carnot engine)

A *relative efficiency* can be defined by comparing the work of the real refrigeration cycle to that of the Carnot

$$\eta_{rc} = \frac{W_{\text{Carnot cycle}}}{W_{\text{refrigeration cycle}}} = \frac{\text{cop}_{\text{refrigeration cycle}}}{\text{cop}_{\text{Carnot pump}}} \quad (14-5)$$

The relative efficiency is always less than unity. In computing this efficiency, the work of the Carnot cycle should be based upon the temperatures of the refrigerated space and the cooling medium. If, instead, the relative efficiency is computed from the temperatures of heat addition and rejection within the cycle, then the system is not penalized for the presence of the irreversible temperature differences that actually are present.

**Example 1.** A Carnot cycle, using steam as the refrigerant, is to operate between 80 F (atmospheric) and 40 F. Assume that the quality of the vapor is 0.80 at the end of isentropic compression (state  $d$  in Fig. 14-1) and that the steam is condensed to saturated liquid (state  $a$  Fig. 14-1). Compute the cop, horsepower required per ton of refrigeration, and the work of each process (all to be flow processes).

**Solution.** By Eq. (14-4),

$$\text{cop} = \frac{T_A}{T_R - T_A} = \frac{500}{540 - 500} = 12.5 \quad \text{Ans}$$

And by Eq. (14-3),

$$\text{Hp/ton} = \frac{4.71}{\text{cop}} = \frac{4.71}{12.5} = 0.378 \text{ hp/ton refrigeration} \quad \text{Ans}$$



The properties at each state of the cycle can be obtained from the Steam Tables and by calculation (letters correspond to Fig 14-1)

$h_a = 48.02$ Btu/lb <sub>m</sub>	$x_a = 0.0$	$v_a = 0.01608$ ft <sup>3</sup> /lb <sub>m</sub>
$h_b = 46.6$	$x_b = 0.0359$	$v_b = 87.9$
$h_c = 824.1$	$x_c = 0.761$	$v_c = 1860$
$h_d = 886.9$	$x_d = 0.80$	$v_d = 506.5$
$s_a = 0.0932$ Btu/lb <sub>m</sub> F	$p_a = 0.5069$ psia	
$s_b = 0.0932$	$p_b = 0.12170$	
$s_c = 1.6474$	$p_c = 0.12170$	
$s_d = 1.6474$	$p_d = 0.5069$	

The work of compression is

$$-W_{cd} = h_d - h_c$$

$$W_{cd} = -(886.9 - 824.1) = -62.8 \text{ Btu/lb}_m \quad \text{Ans}$$

The work of expansion is

$$-W_{ab} = h_b - h_a$$

$$W_{ab} = -(46.6 - 48.02) = +1.42 \text{ Btu/lb}_m \quad \text{Ans}$$

Note that the work obtained in the expansion process is but a small fraction of the work that must be supplied for the compression process.

This example indicates that steam would be a particularly undesirable refrigerant for these temperature limits. The pressures throughout the system are far below atmospheric so that the prevention of air leakage into the system would undoubtedly be a difficult if not impossible task. Compared with other refrigerants the specific volumes at *c* and *d* are large, and this would require a large compressor displacement. For these reasons it would be highly impractical if not impossible to use steam as the working fluid for this cycle (but see Art 14-6).

**14-3. The Vapor-compression Cycle.** Although the Carnot heat pump with a vapor and flow processes is a practical cycle (Art 12-2), a mechanical simplification is achieved by substituting a throttling valve for the expansion machine. This substitution is desirable because, in most instances, the small amount of work that could be obtained (Example 1) from an expansion engine would not justify the added complication and expense. In Fig 14-3, the elements of the vapor-compression cycle are illustrated. The saturated-liquid refrigerant at state *a* is throttled through an *expansion valve* (orifice) to the lower pressure at state *b*. This is a constant-enthalpy process and the temperature of the refrigerant falls to the saturation temperature at the final pressure because of the latent heat demanded by the partial vaporization. The refrigerant is then further vaporized in the evaporator (*bc*) by cooling a flow system of brine (or air). The wet vapor at state *c* is drawn into the compressor and compressed to a temperature  $T_s$  such that the available cooling medium can condense the vapor in the condenser (*da*). The cycle is thus completed.

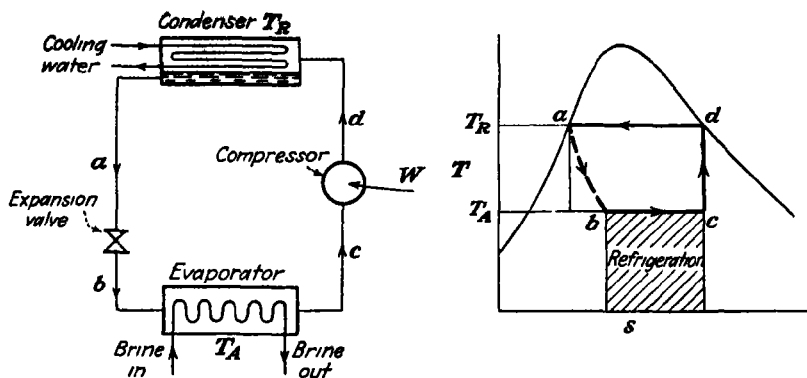


FIG 14-3 Elements of the vapor-compression refrigeration cycle

In the real system, temperature differences will exist and all the processes will be irreversible. Figure 14-4\* depicts some of these effects. In Fig 14-4a, the temperature  $T_A$  at the end of the throttling process ( $ab$ ) is lower than the temperature  $T'_A$  of the cold body. The real compression process is irreversible, and the final state  $d$  lies (most

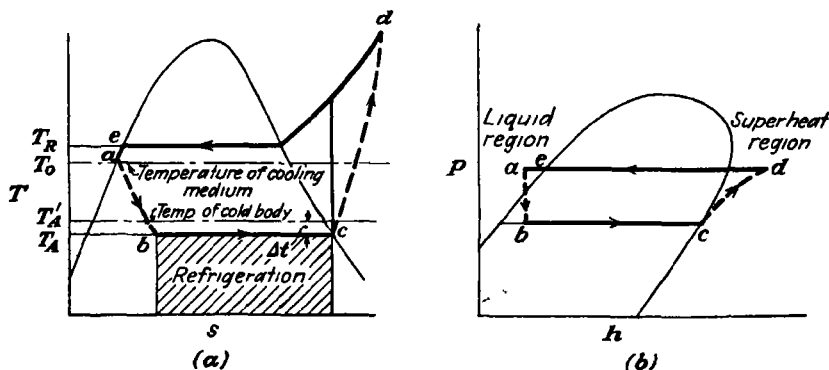


FIG 14-4 Irreversibilities in the vapor-compression refrigeration cycle

often) in the superheat region at a temperature above  $T_R$ . The gas is cooled and condensed in the condenser while the saturated liquid ( $e$ ) is subcooled to a temperature ( $a$ ) quite close to that of the cooling medium,  $T_0$ . In either the real or the ideal system and for a particular refrigerant, the pressure in the condenser is controlled by the temperature of the available coolant while the pressure in the evaporator is determined by the desired refrigeration temperature.

The rate of vaporization of the refrigerant in the evaporator will

\* In Fig 14-4 both the  $Ts$  and the  $ph$  diagrams for the cycle are shown, and in subsequent work in this chapter the  $ph$  diagram will frequently be used.

depend on the temperature difference ( $\Delta t$ , Fig. 14-4a) and also on the time and surface available for transfer of heat from the refrigerated medium. The refrigerant entering the compressor may be wet or dry vapor, the state being controlled by the method of vapor take-off from the evaporator as well as by the mass flow rate, which is governed by a control mechanism on the expansion valve. The compression is said to be *wet*, *partially dry*, or *dry* depending on the relative position of the compression path to the superheat region<sup>1</sup>. Calculations will show that wet compression gives the highest cop, but dry compression is usually preferred because a greater refrigerating effect can be obtained per unit of mass flow.

In small machines the reciprocating-piston type of compressor is frequently used although for low-pressure (and therefore large-volume) work a centrifugal or a rotary compressor has the advantage of being able to handle a greater mass flow rate for a given physical size.

**Example 2:** Determine the condenser and evaporator pressures for carbon dioxide, methyl chloride, and ammonia under the same conditions as in Example 1.

**Solution** The temperature in the condenser is 80 F and in the evaporator is 40 F. The saturation pressures corresponding to these temperatures are as follows (Figs. III, IV, and Table XV, Appendix)

Fluid	Saturation pressure at 40 F, psia	Saturation pressure at 80 F, psia
Carbon dioxide, CO <sub>2</sub>	568	969
Methyl chloride, CH <sub>3</sub> Cl	43 25	86 26
Ammonia, NH <sub>3</sub>	73 32	153

Although the pressures in the CO<sub>2</sub> system are extremely high, it would be found that the specific volume of gas is low and therefore the size of equipment is small (Table 14-1).

In analyzing the flow processes of the vapor-compression cycle, the following quantities may be calculated (all subscripts refer to Fig. 14-4):

#### *Expansion Valve*

$$\begin{aligned}
 Q - W &= \Delta h = 0 \\
 h_a &= h_b \\
 h_a &= (h_f + xh_{fg})_b
 \end{aligned} \tag{14-6}$$

<sup>1</sup> If the compression path lies entirely within the superheat region, the compression is dry, if the path lies entirely within the two-phase region, the compression is wet.

*Evaporator*

$$Q - W = \Delta h \quad \text{and} \quad W = 0$$

$$Q_A = h_c - h_b \quad (14-7)$$

*Compressor*

$$Q - W = \Delta h$$

$$W_{cd} = -(h_d - h_c) + Q_{cd} \quad (14-8)$$

( $Q$  rejected is negative, by convention.)

If compression is isentropic,

$$W_{cd} = -(h_d - h_c) \quad (14-9)$$

*Condenser*

$$Q - W = \Delta h \quad \text{and} \quad W = 0$$

$$Q_R = h_a - h_d \quad (14-10)$$

*Coefficient of Performance*

$$\text{cop} = \frac{Q_A}{-W} = \frac{h_c - h_b}{(h_d - h_c) - Q_{cd}} \quad (14-11)$$

*Mass Flow Rate of Refrigerant per Ton of Refrigeration*

$$m = \text{lb}_m/\text{min ton} = \frac{200 \text{ Btu/min ton}}{Q_A \text{ Btu/lb}_m} = \frac{200}{h_c - h_b} \quad (14-12)$$

*Compressor Capacity per Ton of Refrigeration*

$$C'_{\text{fm/ton}} = m(\text{lb}_m/\text{min ton})v(\text{ft}^3/\text{lb}_m) = mv \quad (14-13)$$

$v$  = specific volume of refrigerant at compressor inlet

*Horsepower Required per Ton of Refrigeration*

$$\text{Hp/ton} = \frac{12,000 \text{ Btu/hr ton}}{(2544 \text{ Btu/hp-hr})\text{cop}} = \frac{4.71}{\text{cop}} \quad (14-3)$$

**Example 3:** A refrigeration system uses ammonia as the refrigerant. The temperatures in the evaporator and condenser are, respectively, 5 and 86 F, the vapor entering the compressor is saturated, and the liquid entering the expansion valve is saturated, compression is isentropic. For these conditions find (a) the heat and work transfers for each process, (b) the cop, (c) horsepower per ton, (d) ideal cop, (e) relative efficiency, (f) mass flow rate, (g) compressor capacity.

**Solution:** The properties at each state will be found by means of Table XV (Appendix) and by calculation (subscripts correspond to Fig. 14-3, although in this problem state  $d$  lies in superheat region).

$$\begin{array}{lll} p_a = 169.2 \text{ psia} & t_a = 86 \text{ F} & h_a = 138.9 \text{ Btu/lb}_m \\ p_c = 34.27 & t_c = 5 & h_c = 613.3 \\ s_c = 1.3253 \text{ Btu/lb}_m\text{R} & & v_c = 8.150 \text{ ft}^3/\text{lb}_m \end{array}$$

Also,

$$h_b = h_a = 138.9 \text{ Btu/lb}_m \quad (14-6)$$

Since the entropy at state  $d$  is equal to that at  $c$ , interpolation of the superheat values in Table XV shows that

$$p_d = p_a = 169.2 \text{ psia} \quad t_d = 211 \text{ F} \quad h_d = 713.4 \text{ Btu/lb}_m$$

With these values, the work and heat transfers can be found

*a.*

$$\begin{aligned} Q_A = Q_{bc} &= h_c - h_b \\ &= 613.3 - 138.9 = 474.4 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned} \quad (14-7)$$

$$\begin{aligned} Q_R = Q_{da} &= h_a - h_d \\ &= 138.9 - 713.4 = -574.5 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned} \quad (14-10)$$

$$\begin{aligned} W_{cd} &= -(h_d - h_c)_{\text{sc}} \\ &= -(713.4 - 613.3) = -100.1 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned} \quad (14-9)$$

or

$$W_{cd} = Q_A + Q_R$$

*b* The coefficient of performance equals

$$\text{cop} = \frac{Q_A}{-W} = \frac{474.4}{100.1} = 4.74 \quad \text{Ans.}$$

*c* The hp ton<sup>-1</sup> of refrigeration equals

$$\begin{aligned} \text{Hp/ton} &= \frac{4.71}{\text{cop}} \\ &= \frac{4.71}{4.74} = 0.995 \quad \text{Ans} \end{aligned} \quad (14-3)$$

*d* The Carnot or ideal cop equals

$$\begin{aligned} \text{cop} &= \frac{T_A}{T_0 - T_A} \\ &= \frac{464.7}{545.7 - 464.7} = 5.74 \quad \text{Ans} \end{aligned} \quad (14-4)$$

*e* The relative efficiency equals

$$\begin{aligned} \eta_{rc} &= \frac{\text{cop}_{\text{actual}}}{\text{cop}_{\text{Carnot}}} \\ &= \frac{4.71}{5.74} = 0.826 \quad \text{Ans} \end{aligned} \quad (14-5)$$

*f* The mass flow rate per ton of refrigeration is

$$\begin{aligned} m &= \frac{200}{Q_A} \\ &= \frac{200}{474.4} = 0.422 \text{ lb}_m/\text{min ton} \quad \text{Ans} \end{aligned} \quad (14-12)$$

*g* The required compressor capacity is

$$\begin{aligned} C &= mv \\ &= 0.422(8.150) = 3.44 \text{ cfm/ton} \quad \text{Ans.} \end{aligned} \quad (14-13)$$

These values differ somewhat from those shown in Table 14-1 because the two

TABLE 14-1 —COMPARISON OF REFRIGERANTS\*

Refrigerant	<i>M</i>	Latent heat 5 F, $\text{Btu lb}_m^{-1}$	<i>k</i>	Mass flow rate, $\text{lb}_m \text{ min}^{-1} \text{ ton}^{-1}$	Com-pressor capacity, $\text{cfm ton}^{-1}$	Evapo-rator pressure, psia	Con-denser pressure, psia	Pressure ratio	cop	Power, $\text{hp ton}^{-1}$	$\eta_c$
Any fluid, Carnot cycle	17 0	565	1 285	0 422	3 44	34 28	169 2	4 93	5 74	0 821	1 00
<i>Ammonia</i>	44 0	115 3	1 304	3 68	0 99	339	1054	3 12	4 77	0 97	0 83
Carbon dioxide	120 9	69 5	1 14	3 92	5 81	26 5	107 9	4 06	2 56	1 84	0 45
Freon, F-12	50 5	180 7	1 28	1 43	6 8	21 2	94 7	4 5	4 72	1 00	0 82
Methyl chloride	44 1	169 5	1 14	1 40	3 35	43 7	159 0	3 6	4 70	1 00	0 82
Propane	64 1	169 4	1 29	1 39	9 24	11 81	66 6	5 6	4 88	0 97	0 85
Sulphur dioxide									4 74	0 99	0 82

\* For 1 ton of refrigeration, 5 F saturated vapor leaving evaporator, 86 F saturated liquid leaving condenser

superheat states listed in Table XV (Appendix) do not allow precise evaluation of intermediate states

The real cycle contains an irreversible throttling process and, also, varying degrees of superheat. Since these variables are governed by the characteristics of the fluid and not directly by the evaporator or condenser pressure, the cop of different refrigerants will not be the same. In Table 14-1 comparison is made of different refrigerants.

**Example 4:** For the data of Example 3, calculate the work of compression, but assume that the refrigerant is an ideal gas with molecular weight that of ammonia.

**Solution:** The isentropic work to compress a perfect gas in a flow process equals

$$W_{rev} = \frac{kRT_1}{1-k} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - 1 \right] \quad (8-13)$$

And, with values from Table VI (Appendix),

$$\begin{aligned} W_{rev} &= \frac{1.29(1.986)464.7}{(17.024)(-0.29)} [(4.94)^{0.226} - 1] \\ &= -104.2 \text{ Btu/lb}_m \quad \text{Ans} \end{aligned}$$

The answer found in Example 3 was

$$W_{rev} = -100.1 \text{ Btu/lb}_m$$

and the error is 4 per cent. This method can be used when tables of properties are incomplete or not available.

**14-4. Properties of Refrigerants.** It is desirable from practical as well as theoretical considerations that the refrigerant should exhibit certain characteristics. The properties of the ideal refrigerant would show the following qualities (compare with those for an ideal heat-engine fluid, Art. 12-4):

1. The latent heat of vaporization should be large, and the heat capacity of the liquid should be small because then the mass flow rate would be low. Note that, the smaller the heat capacity of the liquid, the less will be the vaporization during throttling and therefore the greater the amount of heat that can be abstracted from the cold source.
2. The critical point should be above the highest operating temperature, for then the fluid after compression is close to the two-phase region where condensation can take place at constant temperature; not only are heat-transfer rates better in the two-phase region, but also the irreversibility of a temperature difference is reduced by the constancy of temperature.

- 3 The vapor pressure in the condenser should not be high. High pressures increase design costs and maintenance
- 4 The vapor pressure in the evaporator should be higher than atmospheric pressure. This would prevent air from leaking into the system and so increasing the amount of work that must be supplied to the compressor for a definite amount of refrigeration. Air in the system also adversely affects the rate of heat transfer. The humidity in the air is especially troublesome because the water tends to freeze in the smallest section of the system, the expansion valve.
- 5 The entropy of the saturated vapor should not change markedly with pressure, or else it should increase slightly as the pressure increases because then the refrigerant can enter the condenser as a wet or saturated vapor.
- 6 The properties of the fluid should be conducive to high rates of heat transfer in order that both surface areas and temperature differences can be small in the heat exchangers.
7. The refrigerant should be cheap in cost, stable, nonexplosive, and noncorrosive under all conditions of operation, and nonpoisonous for safety of personnel.

No refrigerant is known that possesses all these properties, but certain fluids have qualities that are particularly suited for special applications. A few of these fluids are listed below and in Table 14-1.

*Anhydrous ammonia* is the most widely used refrigerant because of its high latent heat, moderate pressures, and small compressor capacity (Table 14-1). The evaporator pressure is above atmospheric in the usual installation where temperatures below  $-28^{\circ}\text{F}$  are not demanded. On the debit side, ammonia, while noncorrosive to the ferrous metals, is corrosive toward brass and bronze; ammonia is toxic and, also, irritating to the eyes, nose, and throat (Table XV, Appendix).

*Freon 12* (F-12) (dichlorodifluoromethane  $\text{CCl}_2\text{F}_2$ )\* is used principally in air-conditioning installations and small refrigerators where low toxicity is especially valued. Although its latent heat is low, thus requiring a high mass flow rate, the cop is essentially the same as for ammonia (Table 14-1, and Table XVI, Appendix).

*Methyl chloride* ( $\text{CH}_3\text{Cl}$ ) is quite similar in properties to Freon but is somewhat toxic. It is used principally in commercial refrigerators (Fig IV, Appendix).

\* This structural name indicates that two chlorine and two fluorine radicals have replaced hydrogen in the compound methane ( $\text{CH}_4$ ).



*Carbon dioxide* ( $\text{CO}_2$ ) has been used quite extensively on shipboard as a refrigerant because of its nontoxic properties. However, the high pressures in the system and the low cop have decreased its popularity with the advent of the Freon refrigerants (Fig III, Appendix)

*Sulphur dioxide* ( $\text{SO}_2$ ) is a popular refrigerant for the household refrigerator because of the low pressures in the cycle; it is somewhat more toxic than the other refrigerants.

**14-5. More Complex Vapor-compression Systems.** *a Cascade System* At temperatures lower than  $-20^\circ\text{F}$ , the pressure ratio for the simple refrigeration system is high, and therefore the temperature

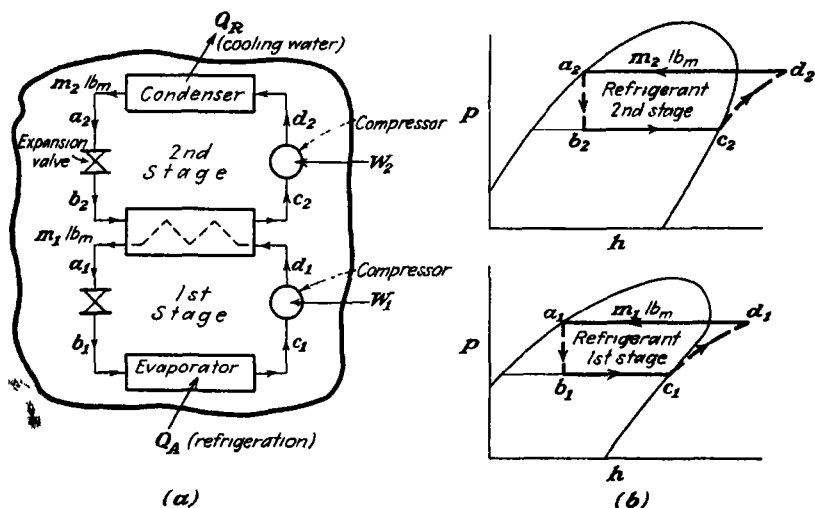


FIG 14-5 Cascade system of refrigeration

after compression may be considerably higher than the condensation temperature since compression occurs in the superheat region (Fig 14-4a). Moreover, if the refrigerant is selected to give a moderate pressure in the evaporator, the condenser pressure will be correspondingly higher, if selection is made to hold low pressures in the condenser, the pressure in the evaporator may be far below atmospheric. These faults can be eliminated in part by using a cascade system (Fig 14-5). In the cascade system two (or more) simple cycles with different refrigerants are operated in series, the condenser of the low-temperature cycle serving as the evaporator for the high-temperature cycle. The cascade system is especially advantageous when refrigeration is demanded at two different temperature levels.

For this system,

$$Q_A = (h_{c1} - h_{b1})m_1$$

$$W = W_1 + W_2 = (h_{c1} - h_{d1})m_1 + (h_{c2} - h_{d2})m_2 \quad (14-14)$$

An energy balance can be made on the intermediate condenser-evaporator

$$m_2(h_{c2} - h_{b2}) = m_1(h_{d1} - h_{a1}) \quad (Q, W = 0)$$

Hence

$$\frac{m_2}{m_1} = \frac{h_{d1} - h_{a1}}{h_{c2} - h_{b2}} \quad (14-15)$$

**Example 5:** A refrigeration system is required to maintain an evaporator temperature of  $-40^\circ\text{F}$  with a condenser temperature of  $80^\circ\text{F}$ . Determine the probable performance of refrigerants Freon F-12 and methyl chloride (a) when used in a simple cycle and (b) when used in a cascade system

**Solution:**

**a Simple Cycle** If Freon F-12 is the refrigerant in a simple cycle between  $-40$  and  $80^\circ\text{F}$ , then, from Table XVI (Appendix),

$$\begin{aligned} h_a &= 26.28 \text{ Btu/lb}_m & p_a &= 98.76 \text{ psia} & t_a &= 80^\circ\text{F (saturated liquid)} \\ h_b &= h_a \\ h_c &= 73.50 \text{ Btu/lb}_m & p_c &= 9.32 \text{ psia} & t_c &= 40^\circ\text{F (saturated vapor)} \\ s_c &= 0.17517 \text{ Btu/lb}_m \text{ F} \end{aligned}$$

Interpolation in Table XVI (Appendix) shows that, after isentropic compression,

$$h_d = 91.58 \text{ Btu/lb}_m \quad p_d = 98.76 \text{ psia} \quad t_d = 110^\circ\text{F (superheated vapor)}$$

With this data,

$$\begin{aligned} W &= h_c - h_d = 73.50 - 91.58 = -18.08 \text{ Btu/lb}_m & \text{Ans} \\ Q_A &= h_c - h_b = 73.50 - 26.28 = 47.22 \text{ Btu/lb}_m & \text{Ans} \\ \text{cop} &= \frac{Q_A}{-W} = \frac{47.22}{18.08} = 2.61 & \text{Ans} \\ \text{Hp/ton} &= \frac{4.71}{\text{cop}} = \frac{4.71}{2.61} = 1.8 \text{ hp/ton} & \text{Ans} \end{aligned}$$

The properties of methyl chloride are found from Fig. IV (Appendix)

$$\begin{aligned} h_a &= 44.36 \text{ Btu/lb}_m & p_a &= 86.26 \text{ psia} & t_a &= 80^\circ\text{F (saturated liquid)} \\ h_b &= h_a \\ h_c &= 190.66 \text{ Btu/lb}_m & p_c &= 6.878 \text{ psia} & t_c &= -40^\circ\text{F (saturated vapor)} \\ h_d &= 244.3 \text{ Btu/lb}_m & p_d &= 86.26 \text{ psia} & t_d &= 245^\circ\text{F (superheated vapor)} \end{aligned}$$

And

$$\begin{aligned} W &= h_c - h_d = 190.7 - 244.3 = -53.6 \text{ Btu/lb}_m & \text{Ans} \\ Q_A &= h_c - h_b = 190.7 - 44.4 = 146.3 \text{ Btu/lb}_m & \text{Ans} \\ \text{cop} &= \frac{Q_A}{-W} = \frac{146.3}{53.6} = 2.73 & \text{Ans} \\ \text{Hp/ton} &= \frac{4.71}{\text{cop}} = 1.73 \text{ hp/ton} & \text{Ans} \end{aligned}$$

**b Cascade System** Here methyl chloride will be used in the high-temperature cycle and Freon in the low-temperature cycle. A temperature difference of  $10^\circ\text{F}$

will be assumed to be present in the intermediate heat exchanger The temperature range for each refrigerant will be arbitrarily set at

Freon	-40 to +20 F
Methyl chloride	+10 to +80 F

With Freon F-12

$h_{a1} = 12.55 \text{ Btu/lb}_m$	$t_{a1} = 20 \text{ F}$	$p_{a1} = 35.75 \text{ psia (saturated liquid)}$
$h_{b1} = h_{a1} = 12.55 \text{ Btu/lb}_m$		
$h_{c1} = 73.5 \text{ Btu/lb}_m$	$t_{c1} = -40 \text{ F}$	$p_{c1} = 9.32 \text{ psia (saturated vapor)}$
$h_{d1} = 83.35 \text{ Btu/lb}_m$	$t_{d1} = 40 \text{ F}$	$p_{d1} = 35.75 \text{ psia (superheated vapor)}$

With methyl chloride

$h_{a2} = 44.36 \text{ Btu/lb}_m$	$t_{a2} = 80 \text{ F}$	$p_{a2} = 86.26 \text{ psia (saturated liquid)}$
$h_{b2} = h_{a2} = 44.36 \text{ Btu/lb}_m$		
$h_{c2} = 197.58 \text{ Btu/lb}_m$	$t_{c2} = 10 \text{ F}$	$p_{c2} = 23.6 \text{ psia (saturated vapor)}$
$h_{d2} = 224.0 \text{ Btu/lb}_m$	$t_{d2} = 160 \text{ F}$	$p_{d2} = 86.26 \text{ psia (superheated vapor)}$

The relative mass flow rates of the two cycles are found by Eq (14-15)

$$\frac{m_2}{m_1} = \frac{h_{d1} - h_{a1}}{h_{c2} - h_{b2}} = \frac{83.35 - 12.55}{197.58 - 44.36} = 0.461 \frac{\text{lb}_m \text{ methyl chloride}}{\text{lb}_m \text{ Freon}}$$

With these values,

$$\begin{aligned} Q_A &= m_1(h_{c1} - h_{b1}) = 73.5 - 12.55 = 61.0 \text{ Btu/lb}_m \text{ F-12} \quad \text{Ans} \\ W &= m_1(h_{c1} - h_{d1}) + m_2(h_{c2} - h_{d2}) \\ &= 73.5 - 83.35 + 0.461(197.58 - 224) \\ &= -22 \text{ Btu/lb}_m \text{ F-12} \quad \text{Ans} \\ \text{cop} &= \frac{Q_A}{-W} = \frac{61}{22} = 2.77 \quad \text{Ans} \\ \text{Hp/ton} &= \frac{4.71}{\text{cop}} = \frac{4.71}{2.77} = 1.70 \text{ hp/ton} \quad \text{Ans} \end{aligned}$$

Comparison of the answers shows that the cascade system has the highest cop. Whether or not this is the maximum value could be decided by making several other trial calculations with different interstage temperatures. Note that the cascade system allows the evaporator pressure to be the higher value given by the Freon while the condenser pressure is the lower value given by the methyl chloride. In this instance the advantage is slight because the choice of refrigerant was limited to the tables in the Appendix, a better combination would be Freon F-22 and sulphur dioxide.

*b Multiple-compression System with Water Intercooling* It has been demonstrated (Art 8-9e) that the work required to compress a gas is directly related to the initial temperature, and that when the pressure ratio is high, two stages (or more) of compression with an intercooler become desirable. But in the refrigeration cycle the cooling medium, which is usually air or water at atmospheric temperature,

is not much cooler than the condenser temperature at the high discharge pressure, and intercooling may be impractical. In Fig 14-6, a two-stage vapor-compression system with intercooling is illustrated. Here the vapor leaving the first-stage compressor can be cooled to some degree ( $de$ ) but not to the saturated-vapor state since the temperature of this state is below the coolant temperature (the temperature of the saturated vapor at pressure  $a$  or  $h$  is presumed to be close to the temperature of the coolant).

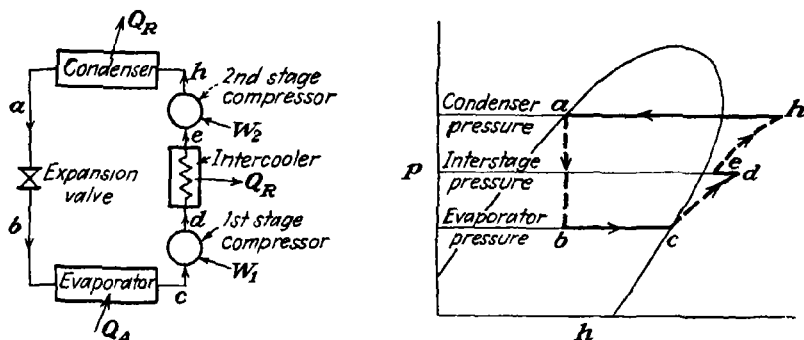


FIG 14-6 Two-stage vapor-compression cycle with intercooler

*c Multiple-compression System with Flash Chamber* As the liquid refrigerant is throttled through the expansion valve, a portion of the liquid is vaporized. This vapor passes through the evaporator without further change in state and therefore without refrigerating the cold source. The compressor, then, must compress the *flash* vapor and also the “working” vapor that is formed by absorption of heat from the cold reservoir. To relieve the compressor of the flash vapor, a two-stage system and *flash chamber* are used (Fig 14-7). Here the liquid is expanded ( $ab$ ) to the intermediate pressure and the flash vapor ( $j$ ), which is useless for refrigeration purposes, passes to the second stage where it is compressed back to the condenser pressure.<sup>1</sup> The liquid portion of the refrigerant in the flash chamber passes through

<sup>1</sup> Although  $(1 + m)$  lb<sub>m</sub> of refrigerant undergoes the throttling process represented by path  $ab$  in Fig 14-7b, the sequence of states visited by 1 lb<sub>m</sub> of the fluid lies along the saturated liquid line  $ac$ , the sequence of states visited by  $m$  lb<sub>m</sub> of the fluid in the same process is not so readily described because at each pressure the state is changing from that of saturated liquid to that of saturated vapor. Thus, the mechanical separation process that divides the two-phase mixture at  $b$  into saturated liquid ( $c$ ) and saturated vapor ( $j$ ) cannot be shown on a property diagram. In effect,  $m$  lb<sub>m</sub> of refrigerant passes through the cycle  $ajka$  while 1 lb<sub>m</sub> passes through the cycle  $acdehka$ .

the second expansion valve and drops to the final pressure ( $cd$ ). Thus, the final state  $d$  of the fluid is at a lesser quality than  $b'$ , a state that would have been attained by a single expansion to the evaporator pressure. Less work need be supplied since the flash vapor removed at the intermediate pressure ratio need only be compressed over a part of the pressure ratio

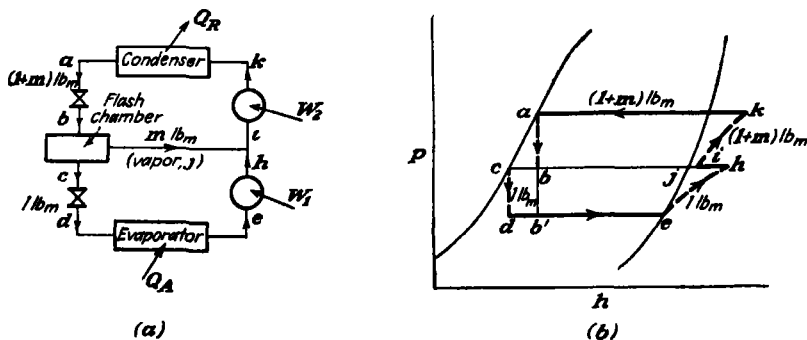


FIG 14-7 Two-stage vapor-compression cycle with flash chamber

For this system, with calculations based upon 1 lb<sub>m</sub> of refrigerant through the evaporator, and  $m$  lb<sub>m</sub> of flash vapor,

$$Q_A = (h_e - h_d)$$

$$W = W_1 + W_2 = (h_c - h_h) + (1 + m)(h_i - h_k) \quad (14-16)$$

The quantity  $m$  can be determined from an energy balance on the expansion valve and flash chamber

$$(1 + m)h_a = mh_i + h_e \quad (Q, W = 0)$$

$$m = \frac{h_c - h_a}{h_a - h_i} = \frac{x_b}{1 - x_b} \quad (14-17)$$

where  $x_b$  = quality of vapor at state  $b$

In the process of mixing flash vapor with superheated vapor at constant pressure, the superheated vapor is cooled ( $hi$ ) while the saturated vapor is superheated ( $je$ ). An energy balance at the mixing point shows that

$$h_i = \frac{mh_i + h_h}{1 + m} \quad (14-18)$$

**Example 6:** For the data of Example 5, suppose that a two-stage system and flash chamber are used with methyl chloride as the refrigerant. Determine the cop and horsepower per ton of refrigeration. Assume that the intermediate pressure has the same value as for methyl chloride in (b) of Example 5

**Solution:** With data from Example 5 and Fig. IV (Appendix) but with subscripts from Fig. 14-7,

$$\begin{array}{lll}
 h_a = 44.36 \text{ Btu/lb}_m & p_a = 86.26 \text{ psia} & t_a = 80 \text{ F (saturated liquid)} \\
 h_b = h_a & p_b = 23.6 \text{ psia} & t_b = 10 \text{ F} \\
 h_c = 18.04 \text{ Btu/lb}_m & h_{f,c} = 179.54 \text{ Btu/lb}_m & t_c = 10 \text{ F (saturated liquid)} \\
 h_1 = 197.58 \text{ Btu/lb}_m & & \text{(saturated vapor)} \\
 h_d = h_c & & \\
 h_e = 190.66 \text{ Btu/lb}_m & p_e = 6.878 \text{ psia} & t_e = -40 \text{ F (saturated vapor)} \\
 h_h = 213.5 \text{ Btu/lb}_m & p_h = 23.6 \text{ psia} & t_h = 90 \text{ F (superheated vapor)}
 \end{array}$$

The quantity  $m$  equals

$$\begin{aligned}
 m &= \frac{h_c - h_a}{h_a - h_1} \\
 &= \frac{18.04 - 44.36}{44.36 - 197.58} = 0.1715 \frac{\text{lb}_m \text{ flash vapor}}{\text{lb}_m \text{ liquid to evaporator}}
 \end{aligned} \quad (14-17)$$

The enthalpy at  $z$  equals

$$\begin{aligned}
 h_z &= \frac{mh_1 + h_h}{1 + m} \\
 &= \frac{0.1715(197.58) + 213.5}{1.1715} = 211 \text{ Btu/lb}_m
 \end{aligned}$$

The vapor at state  $z$ , with enthalpy of  $211 \text{ Btu lb}_m^{-1}$  and pressure of  $23.6 \text{ psia}$ , is isentropically compressed to  $86.26 \text{ psia}$ . From Fig. IV (Appendix),

$$h_k = 241.25 \text{ Btu/lb}_m \quad p_k = 86.26 \text{ psia} \quad t_k = 233 \text{ F (superheated vapor)}$$

Then,

$$\begin{aligned}
 Q_A &= (h_e - h_d) = 190.66 - 18.04 = 172.62 \text{ Btu/lb}_m \\
 W &= (h_e - h_h) + (1 + m)(h_z - h_k) \\
 &= 190.66 - 213.5 + 1.1715(211 - 241.25) = -58.3 \text{ Btu/lb}_m \\
 \text{cop} &= \frac{Q_A}{-W} = \frac{172.62}{58.3} = 2.96 \quad \text{Ans} \\
 \text{Hp/ton} &= \frac{4.71}{\text{cop}} = \frac{4.71}{2.96} = 1.59 \text{ hp/ton} \quad \text{Ans}
 \end{aligned} \quad (14-16)$$

Thus, the performance of the cycle has been improved by the flash chamber

*d Multiple-compression System with Intercooler—Closed Subcooler*  
Figure 14-8 illustrates a system that employs intercooling with refrigerant to reduce the work of the second-stage compressor and also to subcool the liquid flowing to the second expansion valve and evaporator. In this system  $m \text{ lb}_m$  of refrigerant pass through the auxiliary expansion valve to the intercooler while  $1 \text{ lb}_m$  passes through the main expansion valve to the evaporator.<sup>1</sup>

<sup>1</sup> Here  $m \text{ lb}_m$  of refrigerant pass through cycle  $ab_1ka$  while  $1 \text{ lb}_m$  passes through cycle  $acdeh_1ka$

The quantity  $m$  is determined by an energy balance on the inter-cooler.

$$mh_a + h_a + h_h = (1 + m)h_i + h_c \quad (Q, W = 0)$$

$$m = \frac{h_i + h_c - h_h - h_a}{h_a - h_i} \quad (14-19)$$

In this case  $m$  is not uniquely determined as it was in the flash-chamber cycle, various amounts can be bled from the main stream to control the state at  $i$

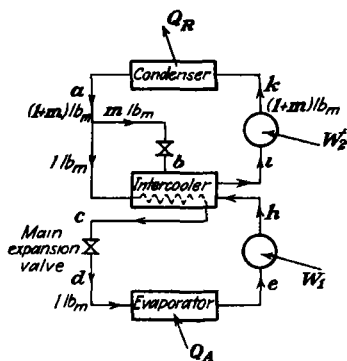


FIG 14-8 Two-stage vapor-compression cycle with closed intercooler

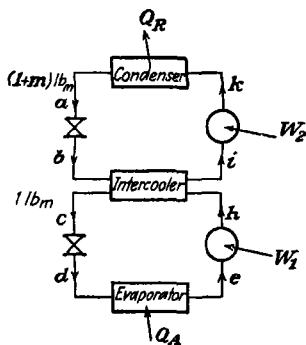
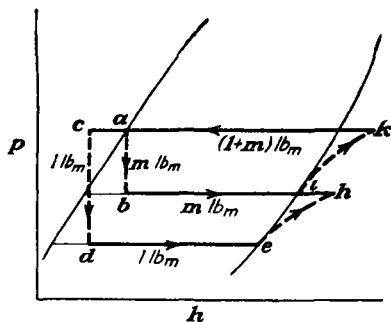
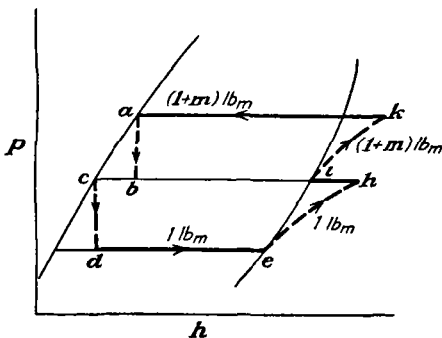


FIG 14-9 Two-stage vapor-compression cycle with open intercooler



*e Multiple-compression System with Intercooler—Open Subcooler*  
Another variation of the two-stage intercooled system is shown in Fig 14-9. Here the flash vapor from throttling is augmented by the vapor formed by cooling the superheated refrigerant from the first-stage compressor. Thus, the intercooler is also a flash chamber. In this system  $m$  lb<sub>m</sub> of refrigerant pass through the cycle  $arka$  while 1 lb<sub>m</sub> of refrigerant passes through the cycle  $acdehka$ .

**14-6. Vacuum Refrigeration.** Water is, without doubt, the safest as well as the cheapest vapor refrigerant although the cycle temperatures must ordinarily be above 32 F. For certain processes, notably air conditioning, low temperatures are not needed and water can be used as the refrigerant although the pressures in the system are sub-atmospheric (Example 1) and the vapor volumes are large. To handle the large volume of refrigerant, an ejector (Art 9-18) is generally used although a centrifugal pump (Art 3-6c) is a possible substitute.

In Fig 14-10, relatively warm water is sprayed into a *flash chamber* that is maintained at a low pressure by an ejector or pump. A small portion of the water flashes into steam, and the latent heat of vaporization so demanded is supplied by the water (the flash chamber is insulated to reduce heat transfer from the surroundings). Thus, the water is cooled to the saturation temperature dictated by the pressure. The chilled water is then pumped to the point where it is required, and the warmed water returned to the flash chamber for cooling.

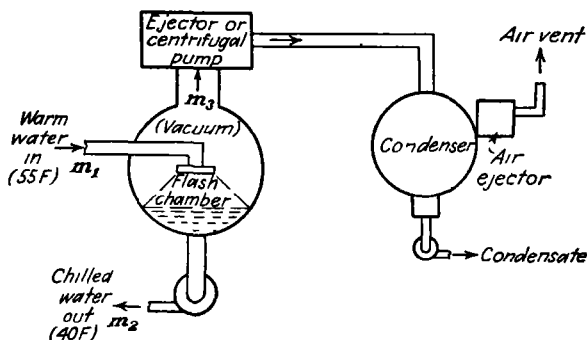


FIG 14-10 Vacuum refrigeration system

The vapor withdrawn from the flash chamber by the ejector or pump is compressed and delivered to the steam condenser (Fig 14-10). Here the pressure, as in the flash chamber, is far below atmospheric, the particular value being determined by the temperature of the available cooling water (Example 1).

The vacuum system, using steam-jet ejectors, has few moving parts because a mechanical compressor is eliminated. This simplification, along with the cheapness and nontoxicity of water, makes up for the inefficiency of the ejector. And if waste steam is available, at pressures above 5 psia (and preferably, much higher), a water-vapor system becomes highly desirable.



An energy balance can be made on the flash chamber to show the refrigeration

$$m_1 h_1 = m_2 h_2 + m_3 h_3 \quad (Q, W = 0)$$

Since

$$m_1 = m_2 + m_3$$

then,

$$m_2(h_1 - h_2) = m_3(h_3 - h_1)$$

And the refrigeration is

$$Q_A = m_2(h_1 - h_2) = m_3(h_3 - h_1) \quad (14-20)$$

**Example 7:** A vacuum system produces 200 gal min<sup>-1</sup> of chilled water at 40 F with return water at 55 F. The vapor leaving the flash chamber has a quality of 0.98, and the temperature in the condenser is 90 F. Determine (a) the pressure in flash chamber and condenser, and pressure ratio, (b) the refrigeration capacity, (c) the amount of make-up water, and (d) the volume of vapor entering ejector.

**Solution:**

a. The vapor pressure of water at 40 F is the pressure in the flash chamber. From the Steam Tables,

$$p = 0.12170 \text{ psia} \quad \text{Ans}$$

The vapor pressure at 90 F is the pressure in the condenser

$$p = 0.6982 \text{ psia} \quad \text{Ans}$$

The pressure ratio equals

$$r_p = \frac{p_{\text{condenser}}}{p_{\text{evaporator}}} = \frac{0.6982}{0.12170} = 5.74 \quad \text{Ans.}$$

b. The mass flow rate equals

$$m_2 = 200 \left( \frac{\text{gal}}{\text{min}} \right) \frac{1}{0.01602} \left( \frac{\text{lb}_m}{\text{ft}^3} \right) 0.1338 \left( \frac{\text{ft}^3}{\text{gal}} \right) = 1,670 \text{ lb}_m/\text{min}$$

And the refrigeration is

$$Q_A = m_2(h_1 - h_2) = 1670(15.02) = 25,100 \text{ Btu/min} \quad \text{Ans}$$

or 125.5 tons      Ans

c. The mass of vapor entering the ejector is found by Eq. (14-20)

$$Q_A = m_3(h_3 - h_1) = 25,100 \text{ Btu/min}$$

where  $h_3 = 8.05 + 0.98(1071.3) = 1058 \text{ Btu/lb}_m$

$$h_1 = 23.07 \text{ Btu/lb}_m$$

Hence,

$$m_3 = \frac{25,100}{1035} = 24.25 \text{ lb}_m/\text{min} \quad \text{Ans.}$$

This is also the quantity of make-up water required

d. The specific volume of the vapor at 40 F is

$$v = 0.016 + 0.98(2.444) = 2.395 \text{ ft}^3/\text{lb}_m$$

and

$$C = mv = 24.25(2,395) = 58,100 \text{ ft}^3/\text{min} \quad \text{Ans.}$$

**14-7. Absorption Refrigeration.** It has already been remarked that the work necessary to compress a liquid is but a small fraction of that required to compress a gas (Art 3-6b). Thus, the work supplied to the refrigeration system could be reduced if the refrigerant were pumped to the condenser pressure as a liquid rather than as a gas. A means of achieving this objective is offered by the *absorption* system (Fig 14-11). Here as in the compression system, the refrigerant passes from condenser to expansion valve to evaporator. But, unlike the compression system, the vapor issuing from the evaporator is dissolved in a cold solvent in the *absorber*, this liquid solution is then pumped into the high-pressure *generator* where the solution is heated. The refrigerant is thus liberated from the solution and passes to the

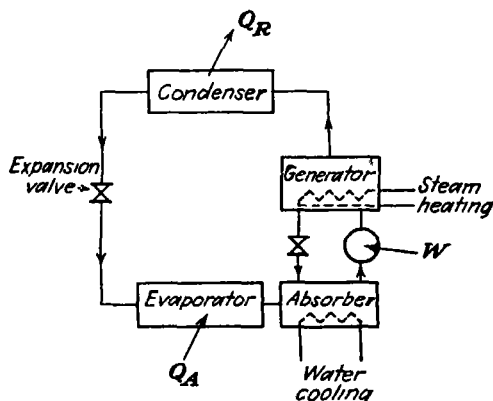


FIG 14-11 Basic elements of the absorption refrigeration system (cycle).

condenser while the solvent returns to the absorber. Of course, the solvent must be able to hold in the cold solution a greater amount of refrigerant than in the hot solution.

An *aqua-ammonia* solution is generally used (ammonia as the refrigerant, water as the solvent) in the absorption system. The ammonia vapor entering the absorber is dissolved in relatively cold (80 to 90 F) water. Heat is liberated in the process and cooling coils are necessary to maintain the low temperature. The cold solution of water and ammonia (called the *strong aqua*) is pumped to the generator where it is heated (200 to 300 F). The hot solution cannot hold as much ammonia as the cold solution; hence, ammonia vapor is liberated and passes to the condenser. The hot and therefore weak solution of

ammonia and water (called the *weak aqua*) is then throttled back to the absorber to be cooled and strengthened

The simple system of Fig 14-11 would deliver not only ammonia but also a large amount of water to the condenser. To improve the performance, a more complicated system must be used. Figure 14-12 shows the ammonia vapor being withdrawn from the evaporator *F* because of the continuous removal of the ammonia vapor in the absorber *G*. The strong aqua from the absorber is pumped (*H*) through a heat exchanger *I* before entering the analyzer *B*. In the analyzer, the strong solution is heated while the gas from the generator is cooled, and, in this cooling, water vapor more than ammonia vapor is condensed. The gas leaving the analyzer thus has a high percentage of ammonia vapor. Sometimes a second cooler, called the *rectifier*

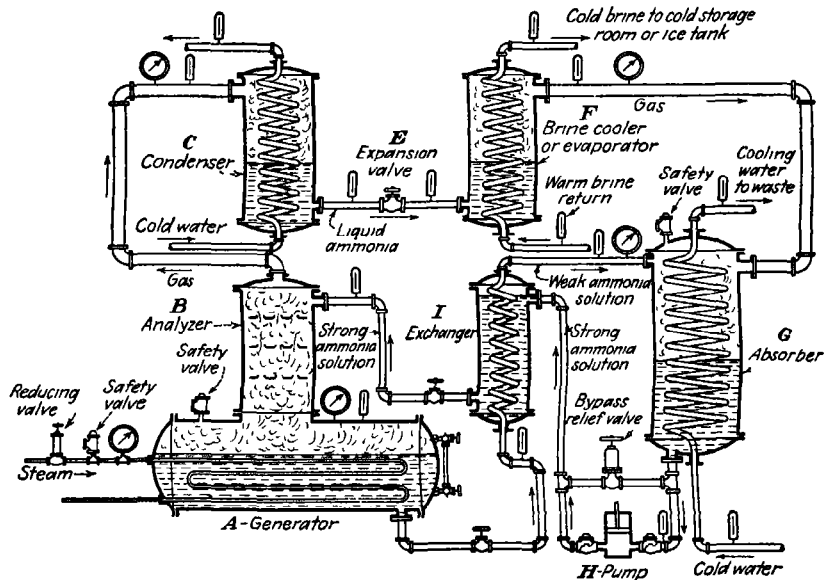


FIG 14-12 An absorption refrigeration system (from Perry, J. H., "Chemical Engineering Handbook," McGraw-Hill Book Co.)

(not shown in Fig 14-12), is placed before the condenser. The rectifier is simply a precondenser that by cooling the gases removes a greater percentage of water than of ammonia. The condensate, or drip, from the rectifier is returned to the generator via the analyzer. The gases finally entering the condenser *C* are thus primarily ammonia.

Although the amount of mechanical energy supplied to the absorption system is small, the amount of thermal energy greatly exceeds the energy requirements of the compression system, and a larger

amount of cooling water is required. For these reasons the absorption system is rarely used unless waste heat is available, say, low-pressure exhaust steam from the power plant. A rational cop is found by dividing the refrigeration by the sum of the work plus the availability of the heat supplied.

**14-8. The Refrigeration Cycle as a Heat Pump.** The heating of buildings is an ever-recurring engineering problem. A building can be heated by burning fuels or by dissipating work, as, for example, when an electric current passes through a resistance heater. Electric-resistance heating, while convenient, is the ultimate degradation of energy, for here available energy is used to produce only heat. Consider that in the power plant a fuel is burned and work is obtained in amount seldom as much as 25 per cent of the heat of combustion of the fuel. Then, the work must have value at least four times that of the heat used to produce the work. Because of this fact, the average building can be heated more cheaply by direct firing of an expensive fuel in an inefficient furnace than by irreversibly using electrical energy that was produced by burning an inexpensive fuel in an efficient furnace.

Even when the electrical energy is produced by water power, the use of such energy for an irreversible heating purpose may be more expensive than direct firing of fuel. The cost of electrical energy includes not only the cost of any fuel used but also the fixed costs of the installation and the distribution costs.

The remedy is to replace the highly irreversible electric-resistance heating process with a process that can at least approach reversibility. Since work in the form of electrical energy can be derived from a heat-engine cycle, then the cycle can be reversed and heat obtained by supplying work. By this means the ratio of performance is reversed and the amount of heat received can be many times the amount of work added. Consider the familiar Carnot cycle of Fig 14-13. Here, for every unit of heat added to the cycle, work is obtained of amount equal to

$$\begin{aligned} W &= \eta_c Q_A \\ &= \frac{560 - 460}{560} (1) = 0.178 \text{ units} \end{aligned}$$

But this cycle can be reversed to act as a heat pump, work of amount 0.178 unit can be supplied, and 1 unit of heat will be received at the higher temperature. Thus, for the heat pump the *coefficient of performance* is defined as

$$\text{cop} = \frac{\text{heat delivered}}{\text{work supplied}} = \frac{Q_R}{W} \quad (14-21)$$

And for Fig 14-13

$$\text{cop} = \frac{1}{0.178} = 5.61$$

or 5.61 units of heat can be obtained by supplying 1 unit of work to the cycle. Compare this answer with the 1 unit of heat that would be received by direct conversion of electrical energy in a resistance heater.

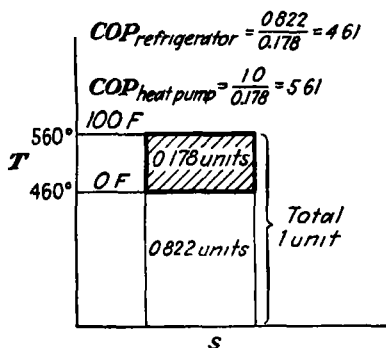


FIG 14-13 The coefficients of performance of the reversed Carnot cycle

Although the heat pump is a refrigeration cycle, the coefficients of performance defined by Eqs (14-2) and (14-21) differ. Comparison shows that

$$\text{cop}_{\text{heat pump}} = \text{cop}_{\text{refrigeration}} + 1 \quad (14-22)$$

It is unfortunate that a heat pump can have two different coefficients of performance.

The reversed heat-engine cycle is called a *refrigerator* (and, also, a *heat pump*) when the evaporator is used for cooling purposes as shown in Fig 14-14a, the same cycle is called a *heat pump* (but not a refrigerator) when the condenser is used for heating purposes as shown in Fig 14-14b. A combined system that serves as a heat pump in the winter and a cooling system in the summer is illustrated in Fig 14-15. Here the system consists of a heat exchanger *A*, a condenser *B*, an expansion valve *C*, an evaporator *D*, and a compressor (not shown). The refrigerant (Freon F-12) is circulated through compressor, condenser, expansion valve, and evaporator. In the heating cycle the cooling water from the condenser passes through the heat exchanger alone and warms the supply air, which is also humidified by the spray humidifier. The evaporator is supplied with water from a deep well, and therefore the temperature of this water is higher than the outside air temperature. This high-temperature water increases the coefficient

of performance. In the cooling cycle the well water is pumped through the evaporator and cooled to a low temperature, it then enters the heat exchanger, which is now a cooling section. The water leaving the heat exchanger passes through the condenser before returning to the ground. This is an example of a *water-to-water* design, water is used to heat the evaporator and also to cool the condenser.

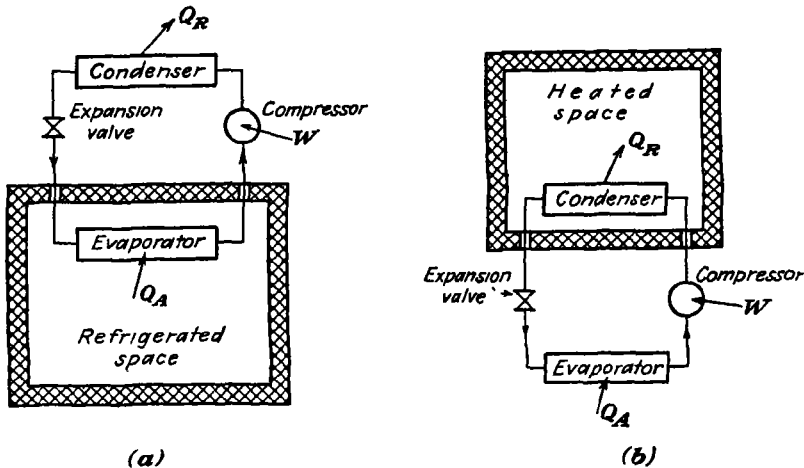
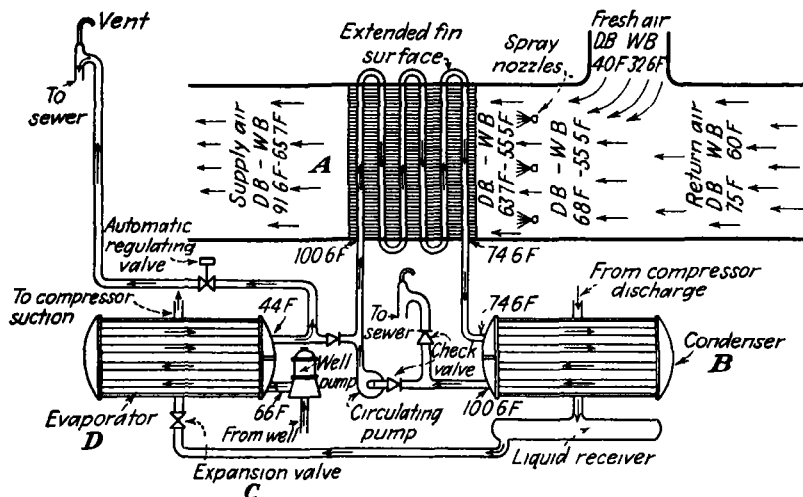


FIG. 14-14 The reversed Carnot cycle as a refrigeration cycle and as a heat pump cycle. (a) Refrigerating. (b) Heating.

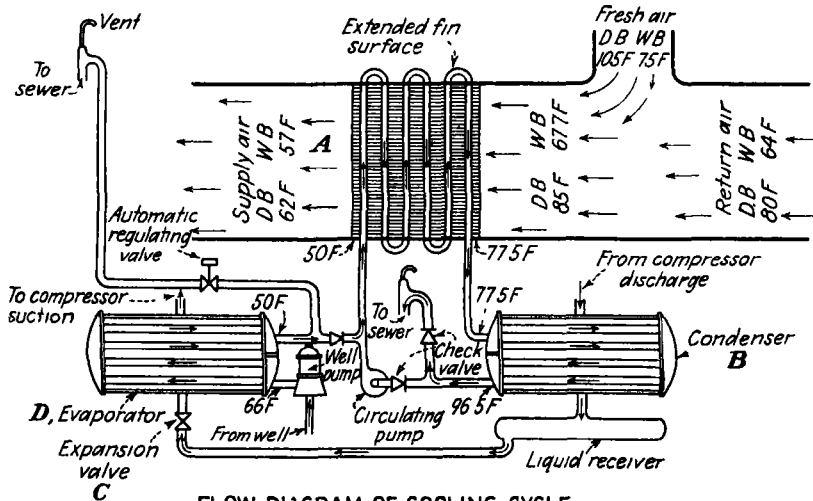
In the installation described in the previous paragraph, water passed over the evaporator of the heat pump and so transferred heat to the cycle. The temperature of the water is frequently above the temperature of the atmosphere because the temperature of the earth does not markedly change with changes in climatic conditions. (In the Chicago area, a well 60 ft in depth will supply water at a temperature of about 50 F.) Where well water is not available, or where withdrawal of water with consequent lowering of the water table is to be avoided, a heat exchanger can be buried in the earth. The heat exchanger can be a vertical U tube running several hundred feet below the surface of the earth. A small quantity of liquid can be circulated through the heat exchanger and the evaporator, the water being heated in the heat exchanger by the relatively warm earth and cooled in the evaporator by the cold refrigerant.

In the winter the surface temperature of the earth decreases in pace with the air temperature as the winter progresses, but the temperature below the surface will lag the air temperature because of the heat capacity and thermal resistance of the earth. Thus, the lowest tem-

perature reached at a depth of 20 ft may occur more than a month after the lowest air temperature of the winter has been experienced Too, under strong sunlight the ground surface temperature may be



FLOW DIAGRAM OF HEATING CYCLE



FLOW DIAGRAM OF COOLING CYCLE

FIG 14-15 Water-to-water combined heat pump and cooling system (from reference 5)

much higher than the air temperature because of the absorption of radiant energy Thus, heat exchangers buried at shallow depths may prove useful

In regions with mild winters where the heating and cooling loads are approximately equal, an *air-to-air system*<sup>1</sup> can be used and the cost of wells or buried heat exchangers can be eliminated. In this heat pump the outside air is used as the source of heat while air is also directly used to cool the condenser. The refrigeration cycle is simplified because air dampers serve as the means of control as illustrated in Fig 14-16. In regions with severe winters, this system is penalized

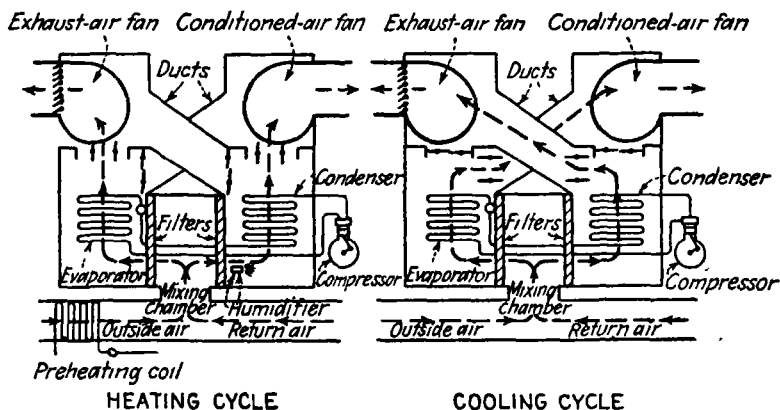


FIG 14-16 Air-to-air heat pump and cooling system.

because the capacity provided for winter heating must be greater than the capacity required for summer cooling, too, frost will form on the evaporator, thus reducing the rate of heat transfer and requiring a defrosting system.

Returning again to the cost factor of the heat pump, recall that the power cycle produces work from heat, and that work in the form of electrical energy can be readily transported. Now if the power cycle were to be reversed, heat would be obtained at a very high temperature but the cost of the heat would be far greater than the original cost to the power plant because all real processes are irreversible and fixed costs and distribution costs must be included. On the other hand, for home heating, heat need be supplied only at moderate temperatures, and therefore the cop of the heat pump will be larger than the cop of the reversed power cycle. In fact, when the thermal efficiency of the power plant is 30 per cent and the cop of the heat pump is 4, the heat obtained from the heat pump is equal to 120 per cent of the heat originally supplied to the power cycle. The heat pump appears to be

<sup>1</sup> Other systems are designated as follows: *earth-to-air* (the earth directly heats the evaporator and air cools the condenser), *water-to-air* (water heats the evaporator and air cools the condenser).



especially advantageous when electricity is obtained from cheap water power or when costs of fuels are high. For these reasons, it is difficult to estimate whether the heat pump can show an economic gain over direct firing; in most cases, direct firing is the cheaper method. An indication of the relative costs is given by Fig 14-17. The heat pump

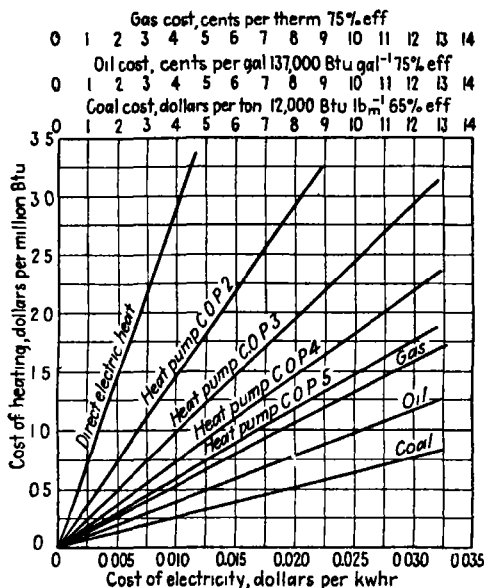


FIG 14-17. Comparative heating costs (from reference 5)

being a refrigeration cycle, however, offers the advantages of both winter heating and summer cooling, and this fact may well prove to be the deciding factor in future installations

### Problems

1. A Carnot reversed cycle is used as a refrigeration system between the standard temperatures of 5 and 86 F. Determine the coefficient of performance and the horsepower per ton of refrigeration.
2. Repeat Example 3, assuming that carbon dioxide is the refrigerant.
3. Repeat Example 3, assuming that the liquid ammonia is subcooled 20 F before entering the expansion valve.
4. For the data of Example 3, assume that the temperature of the refrigerated space is 20 F and the temperature of the cooling water is 70 F, determine the relative efficiency.
5. Ammonia is used as the refrigerant between temperatures of -40 and 80 F. The liquid leaving the condenser is saturated and the vapor entering the compressor is also saturated. Compression is isentropic. Determine the coefficient of performance, the horsepower per ton, and the capacity of the compressor.

6. Repeat Prob 5, assuming that carbon dioxide is the refrigerant
7. With the data of Example 5 and Probs 6 and 5 determine what combination of refrigerants will give the highest coefficient of performance for the cascade system of Example 5?
8. Repeat Example 5, assuming that Freon F-22 and sulphur dioxide are the refrigerants (Data on these refrigerants are to be obtained from a handbook)
9. *a* For the data of Example 3, determine the compressor capacity for a refrigeration capacity of 25 tons  
*b* If a double acting, reciprocating-piston compressor is used with clearance of 0.05 and speed of 100 rpm, what must be the displacement of the compressor (see Art 8-9*d*)?
10. Repeat Example 3, assuming that the isentropic compression efficiency is 0.80 and the process is adiabatic
11. Repeat Example 3, assuming that the vapor entering the compressor contains 10 per cent moisture and compression is isentropic
12. Determine the coefficient of performance and horsepower per ton for a vapor-compression system that uses methyl chloride as the refrigerant between temperatures of 0 and 80 F. The liquid leaving the condenser is subcooled to 70 F, and the vapor entering the compressor is 10 F superheated, isentropic compression efficiency is 0.85 per cent for the adiabatic compression
13. A vapor-compression cycle uses methyl chloride as the refrigerant between evaporator and condenser temperatures of 20 and 100 F, respectively. The horsepower per ton is 1.08, and the liquid leaving the condenser is subcooled to 90 F. Determine the coefficient of performance and the quality of the vapor entering the evaporator
14. Investigate the feasibility of installing an adiabatic expansion engine, with isentropic efficiency of 80 per cent, in the system of Prob 12
15. A refrigeration system, with capacity of 10 tons, is to use Freon F-12 as the refrigerant. The pressures in the evaporator and condenser are to be, respectively, 26 and 121 psia. The liquid at the expansion valve has a temperature of 80 F, the vapor leaving the evaporator is 5 F superheated, the isentropic compression efficiency is 85 per cent, and compression is adiabatic. Determine (*a*) the mass flow rate, (*b*) the coefficient of performance, (*c*) the horsepower per ton of refrigeration, (*d*) the relative efficiency, and (*e*) the displacement of the compressor if the clearance is 0.05
16. Repeat Example 6, assuming that Freon F-12 is the refrigerant
17. Repeat Example 6, assuming that ammonia is the refrigerant
18. Repeat Example 6 for flash-chamber temperatures of 30, 20, and 0 F.
19. A two-stage compression system has a closed subcooler and uses methyl chloride as the refrigerant. The conditions are the same as in Example 6 except that the state at *z* (Fig 14-8) is saturated and the temperature at state *c* is 5 F higher than the ideal temperature. Determine the coefficient of performance and horsepower per ton of refrigeration
20. A two-stage compression system has an open subcooler and uses methyl chloride as the refrigerant. The conditions are the same as in Example 6 except that the state at *z* (Fig 14-9) is saturated. Determine the coefficient of performance and horsepower per ton of refrigeration
21. Repeat Prob 19, assuming that Freon F-12 is the refrigerant
22. Repeat Prob 20 but assume Freon F-12 to be the refrigerant

**23.** A vacuum system with ejector is to produce 50 tons of refrigeration by circulating at 45 F water that is warmed to 55 F. The available cooling water for the condenser can maintain a condensing temperature of 100 F. Determine (a) the mass flow rate of chilled water, (b) the amount of make-up, and (c) the volume of vapor removed from the flash chamber if the vapor is saturated.

**24.** Repeat Prob. 23, assuming that a centrifugal compressor (adiabatic) is to be used with isentropic compression efficiency of 65 per cent. Determine the coefficient of performance and horsepower per ton of refrigeration.

**25.** A Carnot heat pump supplies  $80,000 \text{ Btu hr}^{-1}$  of heat at 75 F when the outside temperature is 32 F. Determine the coefficient of performance, the power required to drive the pump, and the power required for electric-resistance heating (kilowatts).

**26.** A vapor-compression system with Freon F-12 as the refrigerant is to be used as a heat pump to supply  $80,000 \text{ Btu hr}^{-1}$  at 75 F. The outside temperature is 32 F, and a 10 F difference is present between evaporator and outside air, and also between condenser and circulating air for heating. The vapor entering the compressor is saturated, the compression is isentropic, the liquid at the expansion valve is saturated. Determine the coefficient of performance and the cost of heating if electricity is supplied at 5 cents per kilowatthour.

### Symbols

$C$	compressor capacity, also, a constant
$\text{cop}$	coefficient of performance
$\text{cfm}$	cubic feet per minute
$F$	Fahrenheit temperature scale
$h$	specific enthalpy
$\text{hp}$	horsepower
$k$	ratio of $c_p$ to $c_v$
$m$	mass, also, mass flow rate in $\text{lb}_m \text{ min}^{-1}$ or $\text{lb}_m \text{ min}^{-1} \text{ ton}^{-1}$
$M$	molecular weight
$p$	pressure
$Q$	heat
$R$	Rankine temperature scale
$\bar{R}$	specific gas constant
$r_p$	pressure ratio
$s$	specific entropy
$T$	absolute thermodynamic temperature
$t$	thermodynamic temperature
$v$	specific volume
$W$	work
$x$	quality of liquid-vapor mixture

### Subscripts

$A$	added
$f$	saturated liquid
$fg$	change from saturated liquid to saturated vapor
$p$	pressure
$R$	rejected
$\text{rev}$	reversible

$rC$	relative to Carnot
$t$	thermal
0	surroundings

## Greek Letters

$\eta_{rC}$	(eta)	relative efficiency
$\eta_t$	(eta)	thermal efficiency

## Suggested References

- 1 "Refrigerating Data Book and Catalogue," American Society of Refrigeration Engineers, New York, 1947
- 2 "Heating, Ventilating, Air Conditioning Guide," American Society of Heating and Ventilating Engineers, New York, 1947
- 3 SPARKS, N R "Theory of Mechanical Refrigeration," McGraw-Hill Book Company, Inc , New York, 1938
- 4 MOYER, J A , and R U FITTZ "Refrigeration," McGraw-Hill Book Company, Inc , New York, 1932
- 5 PENBOD, E B A Review of Some Heat Pump Installations, *Mech Eng* , **69** (No 8), 639-647 (August, 1947). (Bibliography on heat pumps is included in this article.)







## APPENDIX

TABLE I—DEFINITIONS AND CONVERSION FACTORS\*

### Gravitational Acceleration

$$g_0 = \text{standard acceleration of gravity} = 32\,1739 \text{ ft/sec}^2 \\ = 980\,665 \text{ cm/sec}^2$$

$g$  = local acceleration of gravity

*Force*

1 poundal will accelerate 1 lb<sub>m</sub> at rate of 1 ft/sec<sup>2</sup>  
 1 pound force (lb<sub>f</sub>) will accelerate 1 lb<sub>m</sub> at rate of  $g_0$  ft/sec<sup>2</sup>  
 1 pound force (lb<sub>f</sub>) will accelerate 1 slug at rate of 1 ft/sec<sup>2</sup>  
 1 gravitational lb<sub>f</sub> will accelerate 1 lb<sub>m</sub> at rate of  $g$  ft/sec<sup>2</sup>  
 1 dyne will accelerate 1 gram at rate of 1 cm/sec<sup>2</sup>  
 1 kilogram force will accelerate 1 kilogram mass at rate of  $g_0$  cm/sec<sup>2</sup>.

32 1739 poundals/lb <sub>f</sub>	1 lb <sub>f</sub> = 32 1739 poundals
980,665 dynes/kg <sub>f</sub>	1 kg <sub>f</sub> = 980,665 dynes
13,825 dynes/poundal	1 poundal = 13,825 dynes
444,805 dynes/lb <sub>f</sub>	1 lb <sub>f</sub> = 444,805 dynes
980 665 dynes/g <sub>f</sub>	1 g <sub>f</sub> = 980 665 dynes

## Length

1 cm = 0.01 meters = 0.3937 in  
 1 in = 2.54000 cm  
 1 ft = 12 in = 30.4801 cm  
 1 yd = 3 ft  
 1 mile = 5,280 ft = 1.609 km  
 1 nautical mile = 6,080.27 ft  
 1 meter = 39.37 in  
 1 mile/hour (mph) = 88 ft/min = 44.70 cm/sec  
 1 knot = 1 nautical mile/hr  
 1 cm =  $10^4$  microns =  $10^7$  millimicrons =  $10^8$  angstrom units

\* Selected from various sources

- 1 Eashbach, O W "Handbook of Engineering Fundamentals," John Wiley & Sons Inc , New York, 1936
- 2 Perry, J H "Chemical Engineers' Handbook," McGraw-Hill Book Company, Inc , New York, 1941
- 3 Marks, L S "Mechanical Engineering Handbook," McGraw-Hill Book Company, Inc New York, 1941
- 4 American Petroleum Institute Research Project 44, National Bureau of Standards, Washington D.C. 1944



*Temperature*

$$F = 1.8 C + 32$$

$$C = \frac{F - 32}{1.8}$$

$$\text{degree Rankine (R)} = F + 459.69$$

$$\text{degree Kelvin (K)} = C + 273.16$$

*Mass Equivalents*

$$1 \text{ dram (dr) (avoirdupois)} = 27.34 \text{ g}_m$$

$$1 \text{ ounce (oz) (avoirdupois)} = 16 \text{ dr}$$

$$1 \text{ lb}_m = 453.592 \text{ g}_m = 16 \text{ oz} = 7,000 \text{ grains}$$

$$1 \text{ ton (short)} = 2,000 \text{ lb}_m$$

$$1 \text{ g}_m = 15.432 \text{ grains}$$

$$1 \text{ kg}_m = 2.20462 \text{ lb}_m$$

$$1 \text{ slug} = 32.1739 \text{ lb}_m$$

*Pressure Equivalents*

$$1 \text{ lb}_f/\text{in}^2 = 2.03601 \text{ in Hg at } 32^\circ\text{F} = 2.307 \text{ ft H}_2\text{O at } 4^\circ\text{C} = 0.0703067 \text{ kg}_f/\text{cm}^2$$

$$1 \text{ in Hg} = 33,864 \text{ dynes/cm}^2 = 0.0334211 \text{ atm} = 25.4000 \text{ mm Hg} \\ = 0.491157 \text{ lb}_f/\text{in}^2$$

$$1 \text{ lb}_f/\text{ft}^2 = 4.882 \text{ kg}_f/\text{mm}^2$$

$$1 \text{ kg}_f/\text{cm}^2 = 14.2234 \text{ lb}_f/\text{in}^2$$

$$1 \text{ atm (standard)} = 14.6960 \text{ lb}_f/\text{in}^2 = 760 \text{ mm Hg at } 32^\circ\text{F} \\ = 29.9212 \text{ in Hg at } 32^\circ\text{F} \\ = 1.03323 \text{ kg}_f/\text{cm}^2 = 1,013,250 \text{ dynes/cm}^2 \\ = 33.934 \text{ ft H}_2\text{O at } 60^\circ\text{F}$$

$$1 \text{ bar} = 10^6 \text{ dynes/cm}^2$$

$$\text{Absolute pressure} = \text{barometric pressure} + \text{gauge reading}$$

$$= \text{barometric pressure} - \text{vacuum reading}$$

*Work—Energy—Power*

1 foot poundal is work done by 1 poundal exerted through a distance of 1 ft

1 foot pound<sub>f</sub> (ft lb<sub>f</sub>) is work done by 1 lb<sub>f</sub> exerted through a distance of 1 ft

1 erg is work done by 1 dyne exerted through a distance of 1 cm.

$$10^7 \text{ ergs/joule}$$

$$3,600 \times 10^3 \text{ joules/kwhr}$$

$$3,600 \times 10^{10} \text{ ergs/kwhr}$$

$$2,655,656 \text{ ft lb}_f/\text{int kwhr}$$

$$778.16 \text{ ft lb}_f/\text{IT Btu}$$

$$251.996 \text{ IT cal/IT Btu}$$

$$252.161 \text{ def cal/IT Btu}$$

$$33,000 \text{ ft lb}_f/\text{min hp}$$

$$550 \text{ ft lb}_f/\text{sec hp}$$

$$1 \text{ joule/sec watt}$$

$$44.261 \text{ ft lb}_f/\text{min watt}$$

$$1.000657 \text{ def cal/IT cal}$$

$$1,054.866 \text{ int joules/IT Btu}$$

$$745.578 \text{ int watts/hp}$$

$$2544.48 \text{ IT Btu/hp-hr}$$

$$3412.76 \text{ IT Btu/int kwhr}$$

$$1 \frac{\text{IT Btu}}{\text{lb}_m \text{ F}} = 1 \frac{\text{IT cal}}{\text{g}_m \text{ C}}$$

$$1 \frac{\text{IT Btu}}{\text{lb}_m} = 0.555556 \frac{\text{IT cal}}{\text{g}_m}$$

$$1 \frac{\text{IT cal}}{\text{g}_m} = 1.8 \frac{\text{IT Btu}}{\text{lb}_m}$$

$$1 \frac{\text{def cal}}{\text{g}_m} = 1.79882 \frac{\text{IT Btu}}{\text{lb}_m}$$

$$3.96832(10^{-3}) \text{ IT Btu} = 1 \text{ IT cal}$$

(Btu without prefix is understood to be IT Btu)

*Area*

$$1 \text{ cm}^2 = 0.155 \text{ in.}^2$$

$$1 \text{ in.}^2 = 6.45163 \text{ cm}^2 = 6.94444 (10^{-4}) \text{ ft}^2$$

$$1 \text{ ft}^2 = 929.034 \text{ cm}^2 = 144 \text{ in.}^2$$

*Density*

$$1 \text{ lb}_m/\text{ft}^3 = 0.0160184 \text{ g}_m/\text{cm}^3 = 5.78704 (10^{-4}) \text{ lb}_m/\text{in.}^3$$

*Volume*

$$1 \text{ liter} = 0.0353154 \text{ ft}^3 = 1,000.028 \text{ cm}^3 = 1,000 \text{ ml} = 0.264178 \text{ gal.} \\ = 61.0251 \text{ in.}^3$$

$$1 \text{ ft}^3 = 28.3162 \text{ liters} = 7.48052 \text{ gal}$$

$$1 \text{ gal} = 231 \text{ in.}^3 = 0.133681 \text{ ft}^3 = 3,785.43 \text{ cm}^3$$

$$1 \text{ in.}^3 = 16.3872 \text{ cm}^3$$

*Miscellaneous*

$$\ln_e x = 2.30258 \log_{10} x$$

## CONVERSION FACTORS FOR VISCOSITY†

To convert viscosity in centipoises to viscos- ity in	Poises = $\frac{1 \text{ dyne sec}}{\text{cm}^2}$ = $\frac{1 \text{ g}}{\text{sec cm}}$	$\frac{\text{lb}_m}{\text{ft sec}}$	$\frac{\text{lb}_m}{\text{ft hr}}$	$\frac{\text{lb}_f \text{ sec}}{\text{ft}^2}$ = $\frac{\text{slug}}{\text{ft sec}}$	$\frac{\text{kg}_m}{\text{m sec}}$	$\frac{\text{kg}_f \text{ sec}}{\text{m}^2}$
Multiply by	100	0.000672	2.42	0.000209	$\frac{1}{1,000}$	0.000102

† Reproduced from Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Company, Inc., New York

To convert Saybolt Universal viscosity readings into absolute viscosity readings,

$$\frac{\mu}{\rho} = 2.20 \times 10^{-2} \theta - \frac{1.80}{\theta}$$

$\mu$  = absolute viscosity in poises

$\rho$  = density, grams per cubic centimeter

$\theta$  = time of efflux in seconds (Saybolt Universal seconds)

The above quantities are all to be measured at room temperature

TABLE IIA — APPROXIMATE HEAT-CAPACITY EQUATIONS\*

Gas	Molecular weight	Specific heat at constant pressure ( $c_p$ ), Btu lb <sub>m</sub> <sup>-1</sup> R <sup>-1</sup> $T$ = Rankine degrees	Range R	Maximum deviation from experimental data (%)
N <sub>2</sub>	28 02	$0.227 + 0.0000292T$	720-1900	Less than 1
H <sub>2</sub> O	18 016	$0.433 + 0.0000166T$	720-1900	
CO <sub>2</sub>	44 00	$0.186 + 0.0000625T$	720-1900	Less than 3
CO	28 00	$0.226 + 0.0000321T$	720-1900	Less than 1
H <sub>2</sub>	2 016	$3.35 + 0.000114T$	720-1900	Less than 1
CH <sub>4</sub>	16 03	$0.208 + 0.000561T$	720-1900	
O <sub>2</sub>	32 00	$0.200 + 0.0000353T$	720-1900	Less than 1
Air	28 96	$0.220 + 0.0000306T$	720-1900	Less than 1
C <sub>2</sub> H <sub>18</sub>	114 14	$0.105 + 0.0000486T$	720-1900	

\* TAYLOR, E. S., W. A. LEAHY, and J. R. DIVER: Effect of Fuel-Air Ratio, Inlet Temperature and Exhaust Pressure on Detonation, *NACA Report*, No. 699 (1940)

TABLE IIB — HEAT-CAPACITY EQUATIONS BASED UPON SPECTROSCOPIC DATA\*  
(At zero pressure)

Gas or vapor	Equation $c_p$ in Btu mole <sup>-1</sup> R <sup>-1</sup>	Range R	Maximum error
O <sub>2</sub>	$c_p = 11.515 - \frac{172}{\sqrt{T}} + \frac{1530}{T}$	540-5000	1.1
	$= 11.515 - \frac{172}{\sqrt{T}} + \frac{1530}{T} + \frac{0.05}{1000}(T - 4000)$	5000-9000	0.3
N <sub>2</sub>	$c_p = 9.47 - \frac{3.47 \times 10^3}{T} + \frac{1.16 \times 10^6}{T^2}$	540-9000	1.7
CO	$c_p = 9.46 - \frac{3.29 \times 10^3}{T} + \frac{1.07 \times 10^6}{T^2}$	540-9000	1.1
H <sub>2</sub>	$c_p = 5.76 + \frac{0.578}{1000}T + \frac{20}{\sqrt{T}}$	540-4000	0.8
	$= 5.76 + \frac{0.578}{1000}T + \frac{20}{\sqrt{T}} - \frac{0.33}{1000}(T - 4000)$	4000-9000	1.4
H <sub>2</sub> O	$c_p = 19.86 - \frac{597}{\sqrt{T}} + \frac{7500}{T}$	540-5400	1.8
CO <sub>2</sub>	$c_p = 16.2 - \frac{6.53 \times 10^3}{T} + \frac{1.41 \times 10^6}{T^2}$	540-6300	0.8
CH <sub>4</sub>	$c_p = 4.52 + 0.00737T$	540-1500	1.2
C <sub>2</sub> H <sub>4</sub>	$c_p = 4.23 + 0.01177T$	350-1100	1.5
C <sub>2</sub> H <sub>6</sub>	$c_p = 4.01 + 0.01636T$	400-1100	1.5
C <sub>3</sub> H <sub>8</sub>	$c_p = 7.92 + 0.0601T$	400-1100	Est. 4
C <sub>12</sub> H <sub>26</sub>	$c_p = 8.68 + 0.0889T$	400-1100	Est. 4

\* SWEIGERT, R. L., and M. W. BEARDSLEY: Empirical Specific Heat Equations Based upon Spectroscopic Data, *Georgia School of Technology Bulletin*, 1 (No. 3) (June, 1938)

TABLE IIC — MEAN MOLAL HEAT CAPACITIES AT CONSTANT PRESSURE  
( $c_{pm}$  in Btu mole<sup>-1</sup> R<sup>-1</sup> above 32 F at zero pressure)

Deg F	CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	HO	H <sub>2</sub> O	NO	H <sub>2</sub> S	Air	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
32	8 610	6 960	6 990	6 960	6 860	7 160	7 980	7 160	8 100	6 940	8 240	10 020	10 130
100	8 831	6 966	7 008	6 966	6 883	7 144	7 994	7 158	8 160	6 944	8 361	10 449	10 482
200	9 132	6 970	7 046	6 970	6 916	7 122	8 026	7 143	8 239	6 958	8 622	11 188	10 948
300	9 482	6 986	7 098	6 986	6 936	7 104	8 073	7 152	8 342	6 985	9 047	11 855	11 359
400	9 667	7 016	7 155	7 002	6 950	7 090	8 124	7 173	8 437	7 012	9 431	12 509	11 688
500	9 898	7 036	7 215	7 025	6 962	7 084	8 179	7 196	8 537	7 038	9 824	13 122	11 918
600	10 118	7 068	7 279	7 048	6 972	7 077	8 237	7 233	8 639	7 071	10 224	13 775	12 353
700	10 202	7 102	7 346	7 077	6 977	7 071	8 304	7 277	8 744	7 110	10 580	14 285	12 575
800	10 500	7 138	7 410	7 106	6 983	7 073	8 375	7 321	8 853	7 149	10 942	14 823	12 810
900	10 693	7 177	7 471	7 139	6 988	7 078	8 447	7 366	8 964	7 188	11 298	15 332	13 031
1000	10 902	7 217	7 523	7 169	6 996	7 083	8 511	7 406	9 064	7 224	11 610	15 764	13 221
1100	11 073	7 264	7 582	7 205	7 008	7 089	8 589	7 454	9 184	7 264	11 982	16 266	13 442
1200	11 194	7 299	7 631	7 240	7 018	7 097	8 662	7 496	9 290	7 300	12 301	16 659	13 620
1300	11 292	7 345	7 685	7 274	7 032	7 112	8 748	7 544	9 410	7 344	12 649	17 127	13 817
1400	11 430	7 394	7 733	7 317	7 047	7 134	8 826	7 586	9 518	7 387	12 941	17 584	14 089
1500	11 531	7 441	7 783	7 369	7 065	7 155	8 914	7 634	9 628	7 431	13 260	17 988	14 164
1600	11 642	7 479	7 827	7 399	7 081	7 170	8 996	7 678	9 726	7 469	13 529	18 286	14 317
1700	11 737	7 514	7 865	7 434	7 096	7 188	9 068	7 711	9 818	7 505	13 778	18 584	14 454
1800	11 848	7 574	7 908	7 477	7 115	7 213	9 155	7 750	9 929	7 548	14 082	18 968	14 621
1900	11 947	7 597	7 943	7 517	7 129	7 235	9 234	7 787	10 020	7 583			
2000	12 037	7 635	7 975	7 555	7 147	7 257	9 309	7 825	10 108	7 615			
2100	12 119	7 668	8 007	7 589	7 175	7 278	9 381	7 859	10 198	7 649			
2200	12 190	7 700	8 040	7 620	7 200	7 300	9 450	7 890	10 280	7 680			
2300	12 275	7 740	8 088	7 652	7 227	7 334	9 537	7 924	10 375	7 714			
2400	12 335	7 766	8 116	7 677	7 244	7 356	9 596	7 946	10 434	7 736			
2500	12 423	7 800	8 150	7 718	7 271	7 390	9 681	7 980	10 521	7 768			
2600	12 476	7 818	8 169	7 742	7 289	7 408	9 746	7 998	10 579	7 795			
2700	12 540	7 841	8 192	7 771	7 312	7 431	9 814	8 021	10 654	7 829			
2800	12 601	7 867	8 223	7 794	7 333	7 457	9 878	8 048	10 718	7 853			
2900	12 650	7 895	8 236	7 816	7 356	7 486	9 948	8 075	10 788	7 876			
3000	12 698	7 917	8 256	7 836	7 382	7 506	10 039	8 098	10 853	7 898			
3200	12 805	7 964	8 310	7 892	7 431	7 561	10 157	8 137	10 981	7 945			
3400	12 899	8 000	8 367	7 934	7 479	7 608	10 271	8 178	11 084	7 981			
3600	12 977	8 044	8 413	7 972	7 523	7 662	10 390	8 214	11 193	8 023			
3800	13 053	8 086	8 447	8 012	7 566	7 706	10 511	8 257	11 296	8 058			
4000	13 133	8 122	8 482	8 052	7 622	7 752	10 619	8 291	11 384	8 083			
4200	13 200	8 155	8 527	8 085	7 667	7 795	10 724	8 316	11 464	8 112			
4400	13 258	8 188	8 567	8 110	7 711	7 831	10 812	8 345	11 550	8 149			
4600	13 315	8 223	8 608	8 153	7 756	7 872	10 907	8 368	11 623	8 187			
4800	13 365	8 250	8 639	8 178	7 799	7 904	10 992	8 390	11 689	8 216			
5000	13 415	8 272	8 667	8 208	7 834	7 937	11 079	8 412	11 756	8 242			

TABLE IV.—JOULE'S EQUIVALENT AND THE GAS CONSTANT  $R_0$ 

From time to time various investigators and standardization laboratories have published fundamental definitions of physical constants. The fact that there may be several definitions of one constant may lead to discrepancies in any constants derived therefrom, and this may cause considerable confusion.

In 1929 the First International Steam Tables Conference<sup>1</sup> proposed definitions for the international calorie (IT cal) and the international British thermal unit (IT Btu) in terms of international (int) electrical units

$$1 \text{ IT cal} = \frac{1}{860} \text{ int watt-hour} \quad (a)$$

and

$$1 \frac{\text{IT Btu}}{\text{F lb}_m} = 1 \frac{\text{IT cal}}{\text{C g}_m} \quad (b)$$

Noting that

$$3,600 \text{ joules} = 1 \text{ watt-hour}$$

results in the derived constant

$$4 \, 18605 \frac{\text{int joules}}{\text{IT calories}} \quad (c)$$

Rossini<sup>2</sup> has proposed a defined calorie (def cal)

$$1 \text{ def cal} = 4 \, 18330 \text{ int joules} \quad (d)$$

which is widely used in thermochemistry. From this the derived constant is

$$1 \text{ def cal} = \frac{1}{860 \, 565} \text{ int watt-hour} \quad (e)$$

The relation between the defined calorie and the international calorie is

$$\frac{860 \, 565}{860} = 1 \, 000657 \frac{\text{def cal}}{\text{IT cal}} \text{ or } \frac{\text{def Btu}}{\text{IT Btu}} \quad (f)$$

Because of these different definitions, the values for Joule's constant  $J$  and the gas constant  $R_0$  will have different values in different textbooks, and although the difference is slight, it is quite confusing. For example, older experimental data indicated that

$$1 \, 00032 \text{ absolute joules} = 1 \text{ international joule}$$

With this value and

$$\begin{array}{lll} 860 \frac{\text{IT cal}}{\text{int watt-hour}} & 30 \, 48 \frac{\text{cm}}{\text{ft}} & 1 \, 8 \frac{\text{IT Btu lb}_m^{-1}}{\text{IT cal g}_m^{-1}} \\ 980 \, 665 \frac{\text{cm}}{\text{sec}^2} & 10^7 \frac{\text{ergs}}{\text{joule}} & 3,600 \frac{\text{sec}}{\text{hr}} \end{array}$$

the relationship between the Btu and the ft lb<sub>f</sub> is

$$1 \text{ IT Btu} = \frac{1 \, 00032(10^7)3600}{1 \, 8(860)980 \, 665(30 \, 48)} = 778 \, 28 \text{ ft lb}_f$$

Subsequent experiments<sup>3</sup> indicated that

$$1 \, 00020 \text{ absolute joules} = 1 \text{ international joule}$$

<sup>1</sup> See reference 1

<sup>2</sup> See references 3 and 4

<sup>3</sup> See reference 2

With this newer value it was found that

$$1 \text{ IT Btu} = 778.18 \text{ ft lb}_f$$

More recently<sup>1</sup> the National Bureau of Standards<sup>2</sup> has indicated that

$$1.000165 \text{ absolute joules} = 1 \text{ international joule}$$

With this most recent value, the mechanical equivalent of heat, Joule's equivalent, becomes

$$\begin{aligned} 1 \text{ IT Btu} &= 778.16 \text{ ft lb}_f \\ J &= 778.16 \frac{\text{ft lb}_f}{\text{IT Btu}} \end{aligned} \quad (g)$$

and in textbooks using the defined calorie

$$J = 777.65 \frac{\text{ft lb}_f}{\text{def Btu}} \quad (h)$$

Rossini<sup>3</sup> gives the following value for the gas constant  $R_0$

$$R_0 = 1.98718 \pm 0.00013 \frac{\text{def cal}}{\text{g-mole } ^\circ\text{K}} \quad (i)$$

Equation (i) can be converted into international units by equation (f).

$$R_0 = \frac{1.98718}{1.000657} = 1.98588 \frac{\text{IT cal}}{\text{g-mole } ^\circ\text{K}} \text{ or } \frac{\text{IT Btu}}{\text{mole } ^\circ\text{R}} \quad (j)$$

and from Eq. (g)

$$R_0 = 1545.33 \frac{\text{ft lb}_f}{\text{mole } ^\circ\text{R}} \quad (k)$$

In this text the gas constant is based on the international British thermal unit or as listed below

Values for the Gas Constant  $R_0$

$R_0 = 1545.33 \frac{\text{ft lb}_f}{\text{mole } ^\circ\text{R}}$	$R_0 = 1.98588 \frac{\text{IT cal}}{\text{g-mole } ^\circ\text{K}}$
$R_0 = 10.7315 \frac{\text{psia ft}^3}{\text{mole } ^\circ\text{R}}$	$R_0 = 0.0820544 \frac{\text{atm liters}}{\text{g-mole } ^\circ\text{K}}$
$R_0 = 0.73023 \frac{\text{atm ft}^3}{\text{mole } ^\circ\text{R}}$	$R_0 = 82.0544 \frac{\text{atm ml}}{\text{g-mole } ^\circ\text{K}}$
$R_0 = 1.98588 \frac{\text{IT Btu}}{\text{mole } ^\circ\text{R}}$	$R_0 = 82.0567 \frac{\text{atm cm}^3}{\text{g-mole } ^\circ\text{K}}$

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- 1 First International Steam Tables Conference, *Mech Eng*, **52**, 120-122 (1930)
- 2 BIRGE, R. T. *Rev Modern Phys*, **13**, 233 (1941).
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- 4 MUELLER, E. F., and F. C. ROSSINI. *Am J Phys*, **12**, 1 (1944)
- 5 CURTIS, H. L. *J Research NBS*, **33** (No. 235) (1944) RP 1606
- 6 National Bureau of Standards, Circular C459, May 15, 1947

<sup>1</sup> See references 3 and 5.

<sup>2</sup> See reference 6

<sup>3</sup> See reference 3.

TABLE V—PROPERTIES OF MERCURY VAPOR\*  
( $h$  and  $s$  are measured from 32 F)

Pressure $p$ psia	Temp $t$ , F	Specific volume $v_g$ $\text{ft}^3 \text{lb}_m^{-1}$	Enthalpy, Btu $\text{lb}_m^{-1}$			Entropy, Btu $\text{lb}_m^{-1} \text{R}^{-1}$		
			Saturated liquid $h_f$	Vapor- ization $h_{fg}$	Saturated vapor $h_g$	Saturated liquid $s_f$	Vapor- ization $s_{fg}$	Saturated vapor $s_g$
0.4	402.3	114.5	13.81	128.1	141.9	0.02094	0.1486	0.1696
0.6	426.1	78.23	14.70	127.6	142.3	0.02195	0.1441	0.1660
0.8	443.8	59.71	15.36	127.2	142.6	0.02269	0.1408	0.1635
1.0	458.1	48.45	15.89	126.9	142.8	0.02328	0.1382	0.1615
1.5	485.1	33.14	16.90	126.3	143.2	0.02436	0.1337	0.1580
2	505.2	25.31	17.65	125.8	143.5	0.02514	0.1304	0.1556
3	535.4	17.34	18.78	125.2	144.0	0.02629	0.1258	0.1521
4	558.0	13.26	19.62	124.7	144.3	0.02714	0.1225	0.1497
5	576.2	10.77	20.30	124.3	144.6	0.02780	0.1200	0.1478
6	591.4	9.096	20.87	123.9	144.8	0.02834	0.1179	0.1462
7	605.0	7.882	21.37	123.6	145.0	0.02882	0.1161	0.1450
8	616.8	6.963	21.81	123.4	145.2	0.02923	0.1146	0.1439
9	627.5	6.244	22.21	123.2	145.4	0.02960	0.1133	0.1429
10	637.3	5.661	22.58	122.9	145.5	0.02993	0.1121	0.1420
15	676.5	3.892	24.04	122.1	146.1	0.03124	0.1074	0.1387
20	706.2	2.983	25.15	121.4	146.6	0.03220	0.1041	0.1363
25	730.4	2.429	26.05	120.9	146.9	0.03297	0.1016	0.1345
30	750.9	2.053	26.81	120.4	147.2	0.03360	0.09953	0.1331
35	769.0	1.781	27.49	120.0	147.5	0.03416	0.09774	0.1319
40	784.8	1.576	28.08	119.7	147.8	0.03464	0.09621	0.1308
45	799.3	1.414	28.62	119.4	148.0	0.03507	0.09486	0.1299
50	812.5	1.284	29.11	119.1	148.2	0.03546	0.09364	0.1291
60	836.1	1.086	29.99	118.6	148.6	0.03614	0.09154	0.1276
70	856.6	0.9436	30.75	118.1	148.9	0.03672	0.08976	0.1264
80	874.8	0.8349	31.43	117.7	149.1	0.03725	0.08824	0.1254
90	891.6	0.7497	32.06	117.3	149.4	0.03771	0.08687	0.1245
100	906.9	0.6811	32.63	117.0	149.6	0.03813	0.08565	0.1237
120	934.4	0.5767	33.60	116.4	150.1	0.03887	0.08353	0.1224
140	958.3	0.5012	34.55	115.9	150.4	0.03951	0.08175	0.1212
160	979.9	0.4438	35.35	115.4	150.8	0.04007	0.08019	0.1202
180	999.6	0.3990	36.09	115.0	151.1	0.04058	0.07881	0.1193

\* Reproduced from L. S. Marks, 'Mechanical Engineers' Handbook,' McGraw-Hill Book Company, Inc., New York,

TABLE VI—GAS-CONSTANT VALUES

Gas	Chemical formula	Molecular weight	$R$ ft lb <sub>f</sub> lb <sub>m</sub> R	$c_p$ Btu lb <sub>m</sub> R at 77 F	$c_v$ Btu lb <sub>m</sub> R at 77 F	$k$ $\frac{c_p}{c_v}$
Acetylene	C <sub>2</sub> H <sub>2</sub>	26 02	59 39	0 361	0 285	1 27
Air	..	28 96	53 36	0 240	0 171	1 40
Ammonia	NH <sub>3</sub>	17 024	90 7	0 52	0 404	1 29
Argon	A	39 90	38 73	0 124	0 074	1 68
Butane	C <sub>4</sub> H <sub>10</sub>	58 08	26 61	0 406	0 372	1 09
Carbon dioxide	CO <sub>2</sub>	44 00	35 12	0 201	0 156	1 29
Carbon monoxide	CO	28 00	55 19	0 248	0 177	1 40
Dodecane	C <sub>12</sub> H <sub>26</sub>	170 3	9 074	0 408	0 397	1 03
Ethane	C <sub>2</sub> H <sub>6</sub>	30 05	51 43	0 418	0 352	1 19
Ethylene	C <sub>2</sub> H <sub>4</sub>	28 03	55 13	0 360	0 289	1 25
Helium	He	4 00	386 33	1 25	0 75	1 67
Hydrogen	H <sub>2</sub>	2 016	766 53	3 416	2 431	1 41
Methane	CH <sub>4</sub>	16 03	96 40	0 532	0 408	1 30
Nitrogen	N <sub>2</sub>	28 02	55 15	0 248	0 177	1 40
Octane	C <sub>8</sub> H <sub>18</sub>	114 14	13 54	0 407	0 390	1 04
Oxygen	O <sub>2</sub>	32 00	48 29	0 219	0 157	1 39
Propane	C <sub>3</sub> H <sub>8</sub>	44 06	35 07	0 398	0 353	1 13
Sulphur dioxide	SO <sub>2</sub>	64 07	24 12	0 154	0 123	1 25
Water vapor	H <sub>2</sub> O	18 01	85 6	0 445	0 335	1 33

TABLE VII—CRITICAL CONSTANTS\*

Gas	Sym- bol	$M$ (mo- lecular weight)	$T_c$		$p_c$		$v_c$		$\frac{p_c v_c}{R_c T_c}$
			R	K	Lb/ in <sup>-2</sup>	Atm	Ft <sup>3</sup> mole <sup>-1</sup>	Liters (g mole) <sup>-1</sup>	
Air		28 960	238 4	132 5	546 8	37 2	1 33	0 08302	0 283
Ammonia	NH <sub>3</sub>	17 03	730 01	405 56	1,838 6	111 5	1 16	0 0724	0 243
Butane	C <sub>4</sub> H <sub>10</sub>	58 08	766 8	426 0	529 06	36 0	4 13	0 2576	0 277
Carbon monoxide	CO	28 00	241 5	134 2	508 6	34 6	1 44	0 08989	0 282
Carbon dioxide	CO <sub>2</sub>	44 00	547 6	304 2	1,073	73 0	1 53	0 0955	0 279
Hydrogen	H <sub>2</sub>	2 016	59 9	33 3	188 2	12 8	1 04	0 0649	0 305
Mercury	Hg	200 61	2,078	1,172	2,645 28	180			
Methane	CH <sub>4</sub>	16 03	343 9	191 1	673 3	45 8	1 58	0 0986	0 285
Nitrogen	N <sub>2</sub>	28 02	277 0	126 1	492 32	33 5	1 44	0 0900	0 292
Oxygen	O <sub>2</sub>	32 00	277 9	154 4	730 39	49 7	1 19	0 0744	0 292
Propane	C <sub>3</sub> H <sub>8</sub>	44 06	665 95	369 97	617 38	42 01	3 12	0 195	0 2695
Water	H <sub>2</sub> O	18 02	1,165 1	647 2	3,226	218 5	0 91	0 0568	0 233

\* Data from International Critical Tables, 3, 248-249 (1928), and Bureau of Standards Circular 279 (December, 1925)



TABLE VIII—CONSTANTS FOR EQUATIONS OF STATE

Gas	van der Waals*		Beattie-Bridgeman†					Range, R
	$\frac{a}{\text{atm ft}^6/\text{mole}^2}$	$\frac{b}{\text{ft}^3/\text{mole}}$	$\frac{A_0}{\text{atm ft}^5/\text{mole}^2}$	$\frac{a}{\text{ft}^3/\text{mole}}$	$\frac{B_0}{\text{ft}^3/\text{mole}}$	$\frac{b}{\text{ft}^3/\text{mole}}$	$\frac{10^{-6}c}{\text{ft}^3 \text{ R}^2/\text{mole}}$	
Air	343 8	0 585	334 1	0 309	0 739	-0 176	4 05	230-850
CO	374 7	0 630	344 9	0 419	0 808	-0 111	3 92	
CO <sub>2</sub>	924 2	0 685	1,284 9	1 143	1 678	1 159	61 65	490-670
CH <sub>4</sub>	578 9	0 684	584 6	0 297	0 895	-0 254	11 98	490-850
C <sub>3</sub> H <sub>8</sub>	2,374	1 446	305 8	1 173	2 90	0 688	112 12	
C <sub>4</sub> H <sub>10</sub>	3,675	1 944	456 5	1 948	3 944	1 51	327 02	
H <sub>2</sub>	63 02	0 427	50 57	-0 0811	0 336	-0 698	0 0471	50-850
Hg	5,100	1 070						
H <sub>2</sub> O	1,397 1	0 487						
N <sub>2</sub>	346 0	0 618	344 92	0 419	0 808	-0 111	3 92	
NH <sub>3</sub>	1,076	0 598	613 91	2 729	0 547	3 062	445 6	
O <sub>2</sub>	349 5	0 510	382 53	0 410	0 741	0 0674	4 48	

$$1 \frac{\text{atm ft}^6}{\text{mole}^2} = 14.696 \frac{\text{psi ft}^6}{\text{mole}^2} = 2116.22 \frac{\text{lb}_f \text{ ft}^4}{\text{mole}^2} = 0.003898 \frac{\text{atm (liters)}^2}{\text{g-mole}^2} = 3,898 \frac{\text{atm ml}^2}{\text{g-mole}^2}$$

$$1 \frac{\text{ft}^3}{\text{mole}} = 0.06242 \frac{\text{liters}}{\text{g-mole}} = 62.42 \frac{\text{ml}}{\text{g-mole}}$$

\* Evaluated from critical data in manner of Art 7-8

† Beattie and Bridgeman *Proc Am Acad Arts Sci*, **63**, 229-308 (1928), *J Am Chem Soc*, **50**, 3133 (1928)

TABLE IX—PRESSURE AND TEMPERATURE MEASUREMENTS

## Pressure

A common pressure-measuring device is the *Bourdon tube* gauge, illustrated in Fig A. The gauge consists of a bronze tube flattened into an ellipse and bent

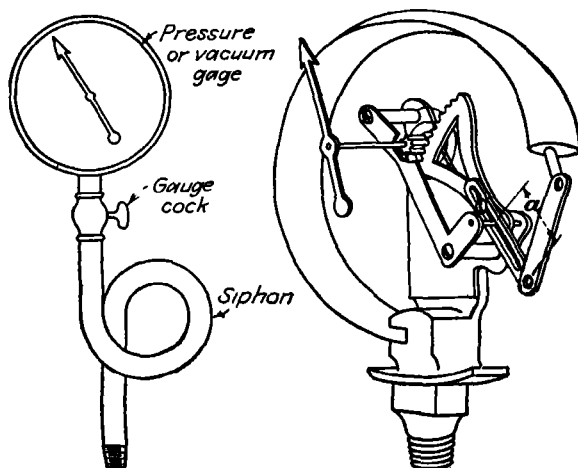


FIG A

into a circular shape. One end of the tube is connected to the region where pressure is to be measured, while the other end is sealed and attached to the sector. The gas or liquid in the system fills the gauge, and the pressure or vacuum causes the bent tube to attempt to regain its original circular cross section. This change tends to straighten the tube, move the sector, and rotate the gear, thus indicating a pressure or a vacuum. By adjusting the distance  $a$  to the best position the gauge will indicate quite accurately over the entire scale. If the distance  $a$  is too short, the gauge will overrun, that is, if it indicates the true pressure, say 20 psi, at one position of the gauge, it will indicate a higher pressure of possibly 40 psi when the true pressure has been increased to 30 psi. Conversely, when distance  $a$  is too long, the gauge will underrun. For these reasons, although most gauges are calibrated over the entire scale, they should not be used for pressures near the beginning or end of travel of the gauge needle.

A *gauge cock* is used to facilitate changing or testing without shutting down the equipment. If small pressure disturbances are present in the medium being measured, the gauge needle will vibrate or oscillate. Such movements can be prevented by slightly closing (throttling) the gauge cock.

A *siphon* is used when the pressure of steam is to be measured. The steam condenses on entering the cold siphon and gauge, hence, the hotter fluid is prevented from too closely approaching the movable parts. On shutdown, the siphon retains the water for use when the system is again operated.

Another form of pressure-measuring instrument is the *manometer*, which is used to measure pressure or differences in pressure. The *U-tube* and *well-type* manometers (Fig. B) are made of glass and partially filled with a liquid of known density. The scale is compensated for changes in level of the liquid in the reservoir with pressure. If one end of the tube (or the well) is connected to a system while the other end is open to the atmosphere, the pressure in the system can be found by equating the pressures above some datum such as  $A-B$  in Fig. B.

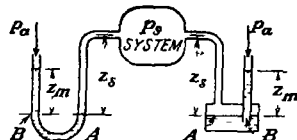


FIG. B

Pressure at  $A$  = pressure at  $B$

$$p_s + z_s \rho_s \frac{g}{g_c} = p_a + \rho_m z_m \frac{g}{g_c}$$

and

$$p_s - p_a = (\rho_m z_m - \rho_s z_s) \frac{g}{g_c}$$

In many cases the fluid in the system is a gas and the density  $\rho_s$  and height  $z_s$  have a negligible effect

$$p_s - p_a \approx \rho_m z_m \frac{g}{g_c}$$

where  $p$  = pressure, lb<sub>f</sub>/ft<sup>2</sup>

$\rho$  = density, lb<sub>m</sub>/ft<sup>3</sup>

$z$  = height, ft

and where subscripts  $a$  = atmospheric

$m$  = manometer fluid

$s$  = system

Another use for the manometer is to measure differences of pressure between two points in the system as in Fig C Proceeding as before

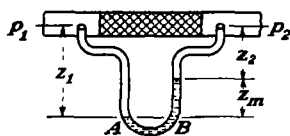


FIG C

Pressure at A = pressure at B

$$p_1 + z_1 \rho_s \frac{g}{g_c} = p_2 + z_2 \rho_s \frac{g}{g_c} + z_m \rho_m \frac{g}{g_c}$$

$$p_1 - p_2 = [-(z_1 - z_2) \rho_s + z_m \rho_m] \frac{g}{g_c}$$

$$= [z_m (\rho_m - \rho_s)] \frac{g}{g_c} \left[ \frac{\text{lb}_f}{\text{ft}^3} \right]$$

If the fluid in the system is a gas,  $\rho_s$  may be negligibly small and

$$p_1 - p_2 \approx z_m \rho_m \frac{g}{g_c}$$

In most cases the pressure difference is desired to be in units of pounds per square inch while the manometer reading is in inches and the fluid used will have a specific gravity  $G$

$$p_1 - p_2 \approx 0.03609 z G \frac{g}{g_c} \text{ lb}_f/\text{in}^2$$

$z$  = manometer height, in

$G$  = specific gravity of manometer fluid at

60 F  $\approx$  39 F referred to water ( $G_{\text{H}_2\text{O}} = 1.0$ )

Another form of manometer is the *inclined tube* or *draft gauge* (Fig D) The inclined-tube manometer is a multiplying device used to measure small pressure differences The reservoir is large in area compared with the area of the inclined tube, hence, variation in the level of the reservoir with respect to the level in the tube is negligible (or the scale is compensated for the error) In commercial instruments the scale on the inclined tube is graduated to read units of inches of water and calibrated to read correctly for a special manometer fluid of definite density Usually, this fluid is not water In the absence of calibration, a pressure balance can be made in the same manner as before, noting that

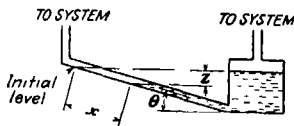


FIG D

$$z = x \sin \theta$$

Temperature

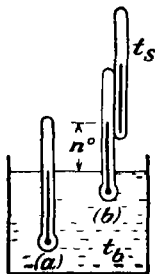


FIG E

The usual mercury thermometer consists of a glass tube with a mercury reservoir at one end and an expansion bulb for overrange protection at the other end It is calibrated by *total immersion* in a constant-temperature bath, as shown in Fig E (a) Total immersion ensures that the glass and mercury will be at bath temperature However, in practice, partial immersion is often necessary [Fig E (b)], and in this case the exposed portion of the thermometer is at a different temperature level than the immersed portion

If the surrounding, or ambient, temperature is lower than the immersed temperature, the portions of mercury and glass exposed to that lower temperature

do not expand to the same point as the portions in the calibrating bath, and therefore a low reading is obtained. The resulting error is approximately

$$\Delta t_c = cn(t_b - t_e)$$

where  $\Delta t_c$  = correction in degrees

$c$  = coefficient of expansion of mercury in glass (The value depends on the type of glass used in making the thermometer. A value of 0.00009 can be assumed approximately true.)

$n$  = number of degrees of mercury not immersed in bath

$t_b$  = temperature of bath (This is the temperature shown by the thermometer, plus the correction. For a close approximation, the indicated temperature is used.)

$t_e$  = temperature of exposed portion of thermometer as indicated by a separate thermometer tied to the exposed portion

Partial-immersion thermometers are made with the immersion level marked on the tube. However, to obtain strict accuracy the exposed portion should be held at the temperature maintained during calibration, and this requirement may be difficult to fulfill.

Commercial grades of thermometers are accurate within  $\pm 2^\circ \text{F}$ . Precision-grade thermometers can be obtained with accuracy of  $\pm \frac{1}{2}^\circ \text{F}$ . For more precise work, thermometers with  $\frac{1}{10}^\circ$  graduations can be obtained with certified calibration data supplied by the manufacturer or standardization laboratory.

The *thermocouple* type of thermometer consists of two wires of dissimilar materials joined together at the ends to form a closed circuit. If one junction of this circuit is at a higher temperature than the other junction, a current will flow because of an electrical potential difference between junctions. This phenomenon, which was first noticed by Seebeck in 1821, is called either the *Seebeck* or the *Peltier* effect. Similarly, whenever a temperature gradient exists in a material, a potential gradient also exists, an effect first predicted by Lord Thomson. The net flow of current in the thermocouple circuit is the resultant of the *Seebeck* and *Thomson* effects, which in turn depend on the materials used in constructing the thermocouple.

To measure this potential, a millivoltmeter can be inserted in the thermocouple circuit between the hot and cold junctions, as shown in Fig. F. The potential indicated by the voltmeter will depend on the combined results of the temperature difference between junctions, the Seebeck effect for the two materials, the Thomson effect for each of the materials, and the resistance of the circuit. Since a circuit of this type is dependent on the resistance of all of its components, it is dependent on the length of the thermocouple. For this reason each circuit should be individually calibrated. When this is done, the millivoltmeter can be graduated directly in degrees.

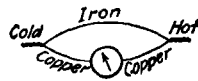


FIG. F

A *potentiometer* can be used to balance the potential of the couple by introducing an equal but opposing potential. In this case the resistance of the circuit should have no effect on the measured potential because no current will flow if perfect balance is obtained. A simple potentiometer circuit is shown in Fig. G and consists of a standard cell, a commercial dry cell, variable resistances, and a galvanometer. The dry cell is calibrated by closing switch A and adjusting

resistance  $R$  until the galvanometer shows no deflection. When this result is obtained, the potential at  $X$  from the battery is equal to the known potential from the standard cell because no current is flowing through the galvanometer.

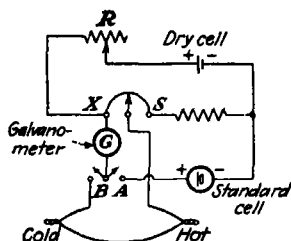


FIG. G

Similarly, the potential gradient through resistance  $S$  will be the same for both the standard and the dry cell. The standard cell is disconnected by throwing the switch to  $B$ , and the potential of the couple is balanced by adjusting the slide arm on resistance  $S$  until no deflection of the galvanometer is present. Resistance  $S$  is graduated either in millivolts or directly in degrees. In the latter case, the couples to be used must be made from definite materials.

Whenever the potentiometer is in use, some current will flow, hence, the battery will eventually be discharged while the potential will gradually decrease. The standard cell is used only infrequently, and it will maintain its calibrated potential for a long period of time while the inexpensive dry cell is easily replaced and calibrated.

Note that the measuring instrument, when inserted in the circuit, will introduce two new junctions. For example, in Fig. G, assume that the instrument is made of copper while the wires to the instrument are made of iron. Then, the junction from iron to copper at one terminal is balanced by a similar junction at the other terminal, while the Thomson effect for the instrument will be zero if the temperature of the instrument is constant.<sup>1</sup> Similarly, the cold junction can be eliminated and the two wires from the hot junction connected directly to the potentiometer. The cold junction in this case is the potentiometer, and the temperature is the room temperature.

Thermocouples are divided into two classes, *noble-* and *base-metal* couples. The noble-metal couples are made of pure platinum, joined to an alloy either of 90 per cent platinum and 10 per cent rhodium or of 87 per cent platinum and 13 per cent rhodium. Such couples are preferred for constancy of calibration over wide periods. Base-metal couples have a low initial cost, but they must be checked at frequent intervals. Usual materials are iron, copper, or chromel used with constantan while the most popular base-metal couple is made of chromel-alumel.

The accuracy of thermocouples depends on the instrument used to measure the potential and, more important, on the condition of the wire and the connection between the two metals. With noble-metal couples an accuracy of  $\pm 2^\circ$  is reasonable, while for base-metal couples the accuracy may be  $\pm 5^\circ$ . These values can be greatly improved by careful calibration, but far greater errors may be present in use.

<sup>1</sup> It can be shown that any number of materials can be inserted into the circuit without effect if the temperature of the inserted materials is constant.

TABLE X—INTERNAL ENERGY OF GASES\*  
(At zero pressure, Btu mole<sup>-1</sup>)

Temp R	O <sub>2</sub>	N <sub>2</sub>	Air	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	$\frac{pv}{778.16}$	C <sub>8</sub> H <sub>18</sub>	C <sub>12</sub> H <sub>26</sub>
520	0	0	0	0	0	0	0	1,033	0	0
536 69	83	81	81	115	101	80	81	1,066	640	911
540	100	97	97	139	122	96	97	1,072	756	1,077
560	200	196	196	280	244	193	196	1,112	1,536	2,188
580	301	295	295	424	357	291	295	1,152	2,340	3,336
600	402	395	395	570	490	390	396	1,192	3,167	4,518
700	920	896	897	1,320	1,110	887	896	1,390	7,668	10,967
800	1,449	1,399	1,403	2,120	1,734	1,386	1,402	1,589	12,768	18,303
900	1,989	1,905	1,915	2,965	2,366	1,886	1,903	1,787	18,471	26,530
1000	2,539	2,416	2,431	3,852	3,009	2,387	2,430	1,986	24,773	35,644
1100	3,101	2,934	2,957	4,778	3,666	2,889	2,954	2,185	31,677	45,648
1200	3,675	3,461	3,492	5,736	4,339	3,393	3,485	2,383	39,182	56,541
1300	4,262	3,996	4,036	6,721	5,030	3,899	4,026	2,582	47,288	68,323
1400	4,861	4,539	4,587	7,731	5,740	4,406	4,580	2,780	55,995	80,994
1500	5,472	5,091	5,149	8,764	6,468	4,916	5,145	2,979	65,303	94,554
1600	6,092	5,652	5,720	9,819	7,212	5,429	5,720	3,178		
1700	6,718	6,224	6,301	10,896	7,970	5,945	6,305	3,376		
1800	7,349	6,805	6,889	11,993	8,741	6,464	6,899	3,575		
1900	7,985	7,393	7,485	13,105	9,526	6,988	7,501	3,773		
2000	8,629	7,989	8,087	14,230	10,327	7,517	8,109	3,972		
2100	9,279	8,592	8,698	15,368	11,146	8,053	8,722	4,171		
2200	9,934	9,203	9,314	16,518	11,983	8,597	9,339	4,369		
2300	10,592	9,817	9,934	17,680	12,835	9,147	9,961	4,568		
2400	11,252	10,435	10,558	18,852	13,700	9,703	10,588	4,766		
2500	11,916	11,056	11,185	20,033	14,578	10,263	11,220	4,965		
2600	12,584	11,682	11,817	21,222	15,469	10,827	11,857	5,164		
2700	13,257	12,313	12,453	22,419	16,372	11,396	12,499	5,362		
2800	13,937	12,949	13,095	23,624	17,288	11,970	13,144	5,561		
2900	14,622	13,590	13,742	24,836	18,217	12,549	13,792	5,759		
3000	15,309	14,236	14,394	26,055	19,160	13,133	14,443	5,958		
3100	16,001	14,888	15,051	27,281	20,117	13,723	15,097	6,157		
3200	16,693	15,543	15,710	28,513	21,086	14,319	15,754	6,355		
3300	17,386	16,199	16,369	29,750	22,066	14,921	16,414	6,554		
3400	18,080	16,855	17,030	30,991	23,057	15,529	17,078	6,752		
3500	18,776	17,512	17,692	32,237	24,057	16,143	17,744	6,951		

TABLE X.—INTERNAL ENERGY OF GASES \*—(Continued)

Temp R	O <sub>2</sub>	N <sub>2</sub>	Air	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	$\frac{pv}{778 \text{ 16}}$	C <sub>2</sub> H <sub>18</sub>	C <sub>12</sub> H <sub>26</sub>
3600	19,475	18,171	18,356	33,487	25,067	16,762	18,412	7,150		
3700	20,179	18,833	19,022	34,741	26,085	17,385	19,082	7,348		
3800	20,887	19,496	19,691	35,998	27,110	18,011	19,755	7,547		
3900	21,598	20,162	20,363	37,258	28,141	18,641	20,430	7,745		
4000	22,314	20,830	21,037	38,522	29,178	19,274	21,107	7,944		
4100	23,034	21,500	21,714	39,791	30,221	19,911	21,784	8,143		
4200	23,757	22,172	22,393	41,064	31,270	20,552	22,462	8,341		
4300	24,482	22,845	23,073	42,341	32,326	21,197	23,140	8,540		
4400	25,209	23,519	23,755	43,622	33,389	21,845	23,819	8,738		
4500	25,938	24,194	24,437	44,906	34,459	22,497	24,499	8,937		
4600	26,668	24,869	25,120	46,193	35,535	23,154	25,179	9,136		
4700	27,401	25,546	25,805	47,483	36,616	23,816	25,860	9,334		
4800	28,136	26,224	26,491	48,775	37,701	24,480	26,542	9,533		
4900	28,874	26,905	27,180	50,069	38,791	25,148	27,226	9,731		
5000	29,616	27,589	27,872	51,365	39,885	25,819	27,912	9,930		
5100	30,361	28,275	28,566	52,663	40,983	26,492	28,600	10,129		
5200	31,308	28,961	29,262	53,963	42,084	27,166	29,289	10,327		
5300	31,857	29,648	29,958	55,265	43,187	27,842	29,980	10,526		
5400	32,607	30,337	30,655	56,569	44,293	28,519	30,674	10,724		

\* LICHY, L C "Internal-Combustion Engines," McGraw-Hill Book Company, Inc, New York, 1939, from data of HERSEY, EBERHARDT, and HOTTEL *Trans SAE*, **31**, 409 (1936)

TABLE XI —ENTHALPY\* FUNCTION  $\frac{\Delta h}{T}$   
(Mean heat capacity)  
(These values are above zero absolute and for the ideal-gas state The unit is the defined calorie per gram mole degree Kelvin, and this unit is equal to the 'defined' Btu per pound mole degree Rankine) (1 000657 def Btu/IT Btu)

Temperature		Carbon		O <sub>2</sub>	H	H <sub>2</sub> O	N <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Temperature K
K	R	Monatomic gas	Solid									
0	0	0	0	0	0	0	0	0	0	0	0	0
200	360	0	0.45086	0.9220	0.8028	0	0	0.9471	0	0	0	200
250	450	0	0.64987	0.9707	0.7772	0	0	0.9495	0	0	0	250
298.16	536.89	0	0.84360	0.9418	0.7577	7.934	0	0.9514	7.5064	8.039	29.30	298.16
300	540	0	0.85111	0.9424	0.7582	7.975	0	0.9515	7.5154	8.042	29.41	300
400	720	5.227	1.2565	0.9681	0.8975	8.059	0	0.9594	8.4555	8.307	33.35	400
500	900	5.164	1.6416	0.9884	0.8860	8.122	0	0.9701	8.8709	8.730	40.93	500
600	1080	5.126		7.1320	0.8619	8.059	0	0.9859	9.6159	9.249	46.40	600
700	1260	5.082		7.2248	0.8272	8.122	0	0.9967	10.3177	9.816	51.54	700
800	1440	5.068		7.3176	0.8218	8.353	0	0.9851	9.6159	10.401	56.26	800
900	1620	5.037		7.4107	0.8423	8.452	7.1432	7.1895	9.9217	10.985	60.61	900
1000	1800	5.048		7.4970	0.8658	8.580	7.2025	7.2565	10.222	11.56		1000
1100	1980	5.041		7.5775	0.8927	8.709	7.2690	7.3238	10.486	12.11		1100
1200	2160	5.035		7.6533	0.9230	8.844	7.3382	7.3898	10.748	12.65		1200
1300	2340	5.030		7.7238	0.9563	8.981	7.3982	7.4538	10.949	13.19		1300
1400	2520	5.026		7.7893	0.9919	9.116	7.4607	7.5179	11.151	13.63		1400
1500	2700	5.022		7.8509	1.0295	9.251	7.5251	7.5725	11.336	14.09		1500
1750	3150	5.016		7.9885	1.2307	9.57	7.6327	7.7033	12.735			1750
2000	3600	5.014		8.1094	1.3558	9.86	7.7497	7.8182	12.912			2000
2250	4050	5.015		8.2193	1.4394	10.16	7.8495	7.9171	12.95			2250
2500	4500	5.019		8.3196	1.5402	10.42	7.9396	8.0028	12.89			2500
2750	4950	5.026		8.4133	1.6379	10.65	8.0131	8.0784	12.80			2750
3000	5400	5.036		8.5000	1.7286	10.86	8.0816	8.1448	12.98			3000
3500	6300	5.062		8.6595	1.8963		8.1986	8.2572	13.29			3500
4000	7200	5.092		8.8038	2.0420		8.2944	8.3487				4000

\* National Bureau of Standards, American Petroleum Institute Research Project 44, Tables 00r/6/30/46, Or 7/31/44, 8/31/46, 1r 8/31/44, 3r 10/31/44



TABLE XII—HEAT OF COMBUSTION\*  
( $\Delta H^\circ$  at 25 C or 77 F)

Compound	Formula	k cal (def) g-mole	IT Btu lb <sub>m</sub>	Reaction
Hydrogen	H <sub>2</sub>	68 3174 57 7979	60957 7 51571 4	H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O (l) H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O (g)
Carbon (graphite)	C	94 0518	14086 8	C (s) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)
Carbon monoxide	CO	67 6361	4343 6	CO (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → CO <sub>2</sub> (g)

Compound	Formula	$\Delta h(h_{fg})^\dagger$ of vaporization, Btu/lb <sub>m</sub>	H <sub>2</sub> O (l) and CO <sub>2</sub> (g)		H <sub>2</sub> O (g) and CO <sub>2</sub> (g)	
			k cal (def)	IT Btu	k cal (def)	IT Btu
			g-mole	lb <sub>m</sub>	g-mole	lb <sub>m</sub>
Methane	CH <sub>4</sub> (g)		212 798	23861	191 759	21502
Ethane	C <sub>2</sub> H <sub>6</sub> (g)		372 820	22304	341 261	20416
Butane	C <sub>4</sub> H <sub>10</sub> (g)	159	687 982	21293	635 384	19665
Pentane	C <sub>5</sub> H <sub>12</sub> (g)	158	845 16	21072	782 04	19499
Heptane	C <sub>7</sub> H <sub>16</sub> (g)	157	1160 01	20825	1075 85	19314
Octane	C <sub>8</sub> H <sub>18</sub> (g)	156	1317 45	20747	1222 77	19256
Benzene	C <sub>6</sub> H <sub>6</sub> (g)	186	789 08	18172	757 52	17446
Decane	C <sub>10</sub> H <sub>22</sub> (g)	154	1632 34	20638	1516 63	19175
Dodecane	C <sub>12</sub> H <sub>26</sub> (g)	154	1947 23	20564	1810 48	19120
Hexadecane	C <sub>16</sub> H <sub>34</sub> (g)	154	2577 00	20472	2398 17	19052

\* First section Table On 4/30/45 5/31/45 API Research Project 44 National Bureau of Standards Second section, Table 1n 3/31/44 4/30/45, API Research Project 44, National Bureau of Standards

† At 25 C and saturation pressure

TABLE XIII.—HEAT OF FORMATION, ABSOLUTE ENTROPY, AND FREE ENERGY OF FORMATION AT 25 C (77 F)\*

Compound	Formula	State	$\Delta H_f^\circ$	$S^\circ$	$\Delta G_f^\circ$
			k-cal (def) g-mole	cal (def) g-mole K	k-cal (def) g-mole
Oxygen	O <sub>2</sub>	gas	0	49 003	0
Hydrogen	H <sub>2</sub>	gas	0	31 211	0
Water†	H <sub>2</sub> O	gas	-57 7979	45 106	-54 6351
		liquid	-68 3174	16 716	-56 6899
Nitrogen	N <sub>2</sub>	gas	0	45 767	0
Carbon	C	graphite, solid	0	1 3609	0
		monatomic gas		37 761	115 509
Carbon monoxide	CO	gas	-26 4157	47 300	-32 8079
Carbon dioxide	CO <sub>2</sub>	gas	-94 0518	51 061	-94 2598
Methane	CH <sub>4</sub>	gas	-17 889	44 50	-12 140
Octane	C <sub>8</sub> H <sub>18</sub>	gas	-49 82	110 82	4 14
		liquid	-59 74	85 50	1 77
Benzene	C <sub>6</sub> H <sub>6</sub>	gas	19 820	64 34	30 989
n-Dodecane	C <sub>12</sub> H <sub>26</sub>	gas	-69 52	147 55	12 33
n-Hexadecane	C <sub>16</sub> H <sub>34</sub>	gas	-89 23	184 28	20 52

\* Table 0p 4/30/45, 1p 4/30/44, 4/30/45, 3p 4/30/44, 4/30/45, 5p 11/30/45, 20p 6/30/46, API Research Project 44, National Bureau of Standards

† The absolute entropy for liquid water at 32 F and 0 08854 psia is 0 8402 Btu lb<sub>m</sub><sup>-1</sup> R<sup>-1</sup>. Therefore, the absolute entropy for H<sub>2</sub>O can be obtained by adding 0 8402 to the Steam Table values

TABLE XIV — ABSOLUTE ENTROPY FOR THE IDEAL GAS STATE\*  
(S° at 1 atm pressure and the temperature indicated, cal (def) g-mole<sup>-1</sup> K<sup>-1</sup>)

Compound	Formula	State	Temperature in degrees Kelvin						
			0	298 16	500	1000	2000	3000	4000
Carbon	C	monatomic gas	0	37 761	40 333	43 778	47 229	49 286	50 798
		graphite, solid	0	1 3609	2 788	5 846			
Oxygen	O <sub>2</sub>	gas	0	49 003	52 723	58 194	64 212	67 968	70 762
Hydrogen	H <sub>2</sub>	gas	0	31 211	34 809	39 704	45 005	48 448	51 030
Water†	H <sub>2</sub> O	gas	0	45 106	49 334	55 598	63 26	68 45	
		gas	0	45 767	49 385	54 509	60 228	63 770	66 338
Nitrogen	N <sub>2</sub>	gas	0	45 767	49 385	54 509	60 228	63 770	66 338
Carbon monoxide	CO	gas	0	47 301	50 927	56 116	61 986	65 459	68 037
Carbon dioxide	CO <sub>2</sub>	gas	0	51 061	56 109	64 331	73 92	80 09	
Methane	CH <sub>4</sub>	gas	0	44 5	49 48	59 21			
Octane	C <sub>8</sub> H <sub>18</sub>	gas	0	110 82	140 35	200 35			
Dodecane	C <sub>12</sub> H <sub>26</sub>	gas	0	147 55	191 57	280 47			

\* Table 00t 6/30/46, 0t 7/31/44, 7/31/46, 1t 8/31/44, 3t 10/31/44, 20t 11/30/45, API Research Project 44, National Bureau of Standards

† The absolute entropy for liquid water at 32 F and 0 08854 psia is 0 8402 Btu lb<sub>m</sub><sup>-1</sup> R<sup>-1</sup>. Therefore, the absolute entropy for H<sub>2</sub>O can be obtained by adding 0 8402 to the Steam Table values

TABLE XV—PROPERTIES OF AMMONIA\*

Sat temp., F	Abs press., psia	Volume, ft <sup>3</sup> lb <sup>m</sup> - <sup>1</sup>		Specific enthalpy and entropy taken from -40 F							
				Specific enthalpy, h		Entropy, s		100 F superheat		200 F superheat	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	h	s	h	s
-40	10 41	0 02322	24 86	0 0	597 6	0 0	1 4242	649 3	1 5353	700 9	1 6261
-30	13 9	0 02345	18 97	10 7	601 4	0 0250	1 4001	654 0	1 5101	706 0	1 6006
-20	18 3	0 02369	14 68	21 4	605 0	0 0497	1 3774	658 3	1 4868	710 7	1 5760
-10	23 74	0 02393	11 5	32 1	608 5	0 0738	1 3558	662 7	1 4647	715 6	1 5531
0	30 42	0 02419	9 116	42 9	611 8	0 0975	1 3352	666 8	1 4439	720 3	1 5317
2	31 92	0 02424	8 714	45 1	612 4	0 1022	1 3312	667 6	1 4400	721 2	1 5277
4	33 47	0 02430	8 333	47 2	613 0	0 1069	1 3273	668 4	1 4360	722 2	1 5236
5	34 27	0 02432	8 150	48 3	613 3	0 1092	1 3253	668 8	1 4340	722 6	1 5216
6	35 09	0 02435	7 971	49 4	613 6	0 1115	1 3234	669 3	1 4321	723 1	1 5196
8	36 77	0 02440	7 629	51 6	614 3	0 1162	1 3195	670 1	1 4281	724 1	1 5155
10	38 51	0 02446	7 304	53 8	614 9	0 1208	1 3157	670 9	1 4242	725 0	1 5115
12	40 31	0 02451	6 996	56 0	615 5	0 1254	1 3118	671 7	1 4205	725 9	1 5077
14	42 18	0 02457	6 703	58 2	616 1	0 1300	1 3081	672 5	1 4168	726 8	1 5039
16	44 12	0 02462	6 425	60 3	616 6	0 1346	1 3043	673 4	1 4130	727 8	1 5001
18	46 13	0 02468	6 161	62 5	617 2	0 1392	1 3006	674 2	1 4093	728 7	1 4963
20	48 21	0 02474	5 910	64 7	617 8	0 1437	1 2969	675 0	1 4056	729 6	1 4925
22	50 36	0 02479	5 671	66 9	618 3	0 1483	1 2933	675 8	1 4021	730 5	1 4889
24	52 59	0 02485	5 443	69 1	618 9	0 1528	1 2897	676 6	1 3985	731 4	1 4853
26	54 90	0 02491	5 227	71 3	619 4	0 1573	1 2861	677 3	1 3950	732 4	1 4816
28	57 28	0 02497	5 021	73 5	619 9	0 1618	1 2825	678 1	1 3914	733 3	1 4780
30	59 74	0 02503	4 825	75 7	620 5	0 1663	1 2790	678 9	1 3879	734 2	1 4744
32	62 29	0 02508	4 637	77 9	621 0	0 1708	1 2755	679 7	1 3846	735 1	1 4710
34	64 91	0 02514	4 459	80 1	621 5	0 1753	1 2721	680 4	1 3812	736 0	1 4676
36	67 63	0 02521	4 289	82 3	622 0	0 1797	1 2686	681 2	1 3779	736 8	1 4643
38	70 43	0 02527	4 126	84 6	622 5	0 1841	1 2652	681 9	1 3745	737 7	1 4609
39	71 87	0 02530	4 048	85 7	622 7	0 1863	1 2635	682 3	1 3729	738 2	1 4592
40	73 32	0 02533	3 971	86 8	623 0	0 1885	1 2618	682 7	1 3712	738 6	1 4575
41	74 80	0 02536	3 897	87 9	623 2	0 1908	1 2602	683 1	1 3696	739 0	1 4559
42	76 31	0 02539	3 823	89 0	623 4	0 1930	1 2585	683 4	1 3680	739 5	1 4542
44	79 38	0 02545	3 682	91 2	623 9	0 1974	1 2552	684 2	1 3648	740 4	1 4510
46	82 55	0 02551	3 547	93 5	624 4	0 2018	1 2519	684 9	1 3616	741 3	1 4477
48	85 82	0 02558	3 418	95 7	624 8	0 2062	1 2486	685 6	1 3584	742 2	1 4445
50	89 19	0 02564	3 294	97 9	625 2	0 2105	1 2453	686 4	1 3552	743 1	1 4412
52	92 66	0 02571	3 176	100 2	625 7	0 2149	1 2421	687 1	1 3521	744 0	1 4382
54	96 23	0 02577	3 063	102 4	626 1	0 2192	1 2389	687 8	1 3491	744 8	1 4351
56	99 91	0 02584	2 954	104 7	626 5	0 2236	1 2357	688 5	1 3460	745 7	1 4321
58	103 7	0 02590	2 851	106 9	626 9	0 2279	1 2325	689 2	1 3430	746 5	1 4290
60	107 6	0 02597	2 751	109 2	627 3	0 2322	1 2294	689 9	1 3399	747 4	1 4260
62	111 6	0 02604	2 656	111 5	627 7	0 2365	1 2262	690 6	1 3370	748 2	1 4231

TABLE XV — PROPERTIES OF AMMONIA \*—(Continued)

Sat temp, F	Abs press, psia	Volume, ft <sup>3</sup> lbm <sup>-1</sup>		Specific enthalpy and entropy taken from -40 F							
				Specific enthalpy, h		Entropy, s		100 F superheat		200 F superheat	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	h	s	h	s
64	115 7	0 02611	2 565	113 7	628 0	0 2408	1 2231	691 3	1 3341	749 1	1 4202
66	120 0	0 02618	2 477	116 0	628 4	0 2451	1 2201	691 9	1 3312	749 9	1 4172
68	124 3	0 02625	2 393	118 3	628 8	0 2494	1 2170	692 6	1 3283	750 8	1 4143
70	128 8	0 02632	2 312	120 5	629 1	0 2537	1 2140	693 3	1 3254	751 6	1 4114
72	133 4	0 02639	2 235	122 8	629 4	0 2579	1 2110	694 0	1 3226	752 4	1 4086
74	138 1	0 02646	2 161	125 1	629 8	0 2622	1 2080	694 6	1 3199	753 3	1 4059
76	143 0	0 02653	2 089	127 4	630 1	0 2664	1 2050	695 3	1 3171	754 1	1 4031
78	147 9	0 02661	2 021	129 7	630 4	0 2706	1 2020	695 9	1 3144	755 0	1 4004
80	153 0	0 02668	1 956	132 0	630 7	0 2749	1 1991	696 6	1 3116	755 8	1 3976
82	158 3	0 02675	1 892	134 3	631 0	0 2791	1 1962	697 2	1 3089	756 6	1 3949
84	163 7	0 02684	1 831	136 6	631 3	0 2833	1 1933	697 8	1 3063	757 4	1 3923
86	169 2	0 02691	1 772	138 9	631 5	0 2875	1 1904	698 5	1 3040	758 3	1 3896
88	174 8	0 02699	1 716	141 2	631 8	0 2917	1 1875	699 1	1 3010	759 1	1 3870
90	180 6	0 02707	1 661	143 5	632 0	0 2958	1 1846	699 7	1 2983	759 9	1 3843
92	186 6	0 02715	1 609	145 8	632 2	0 3000	1 1818	700 3	1 2957	760 7	1 3818
94	192 7	0 02723	1 559	148 2	632 5	0 3041	1 1789	700 9	1 2932	761 5	1 3793
96	198 9	0 02731	1 510	150 5	632 6	0 3083	1 1761	701 5	1 2906	762 2	1 3768
98	205 3	0 02739	1 464	152 9	632 9	0 3125	1 1733	702 1	1 2881	763 0	1 3743
100	211 9	0 02747	1 419	155 2	633 0	0 3166	1 1705	702 7	1 2855	763 8	1 3718
102	218 6	0 02756	1 375	157 6	633 2	0 3207	1 1677	703 3	1 2830	764 6	1 3693
104	225 4	0 02764	1 334	159 9	633 4	0 3248	1 1649	703 8	1 2805	765 3	1 3668
106	232 5	0 02773	1 293	162 3	633 5	0 3289	1 1621	704 3	1 2780	766 1	1 3643
108	239 7	0 02782	1 254	164 6	633 6	0 3330	1 1593	705 0	1 2755	766 9	1 3619
110	247 0	0 02790	1 217	167 0	633 7	0 3372	1 1566	705 5	1 2731	767 6	1 3596
112	254 5	0 02799	1 180	169 4	633 8	0 3413	1 1538	706 1	1 2708	768 3	1 3573
114	262 2	0 02808	1 145	171 8	633 9	0 3453	1 1510	706 6	1 2684	769 1	1 3550
116	270 1	0 02817	1 112	174 2	634 0	0 3495	1 1483	707 2	1 2661	769 8	1 3527
118	278 2	0 02827	1 079	176 6	634 0	0 3535	1 1455	707 7	1 2636	770 5	1 3503
120	286 4	0 02836	1 047	179 0	634 0	0 3576	1 1427	708 2	1 2612	771 3	1 3479
122	294 8	0 02846	1 017	181 4	634 0	0 3618	1 1400	708 6	1 2587	772 0	1 3455
124	303 4	0 02855	0 987	183 9	634 0	0 3659	1 1372	709 1	1 2563	772 8	1 3431
126	312 2	0 02865	0 958	186 3	633 9	0 3700	1 1344	709 6	1 2538	773 5	1 3407
128	321 2	0 02875	0 931	188 8	633 9	0 3741	1 1316	710 0	1 2513	774 2	1 3383

\* IT Btu and lbm, data are mainly from "Heating, Ventilating, Air Conditioning Guide," American Society of Heating and Ventilating Engineers, New York, 1947

TABLE XVI.—PROPERTIES OF DICHLORODIFLUOROMETHANE (F-12)\*

Sat temp, F	Abs press, psia	Volume, ft <sup>3</sup> lb <sub>m</sub> <sup>-1</sup>		Specific enthalpy and entropy taken from -40 F							
				Specific enthalpy, h		Entropy, s		25 F superheat		50 F superheat	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	h	s	h	s
-40	9 32	0 0106	3 911	0 0	73 5	0 0	0 17517	76 85	0 18277	80 25	0 19020
-30	12 02	0 0107	3 088	2 03	74 7	0 00471	0 17387	78 05	0 18147	81 45	0 18890
-20	15 28	0 0108	2 474	4 07	75 87	0 00940	0 17275	79 22	0 18035	82 62	0 18778
-10	19 2	0 0109	2 003	6 14	77 05	0 01403	0 17175	80 48	0 17918	84 01	0 18639
0	23 87	0 0110	1 637	8 25	78 21	0 01869	0 17091	81 71	0 17829	85 26	0 18547
2	24 89	0 0110	1 574	8 67	78 44	0 01961	0 17075	81 94	0 17812	85 51	0 18529
4	25 96	0 0111	1 514	9 10	78 67	0 02052	0 17060	82 17	0 17795	85 76	0 18511
5	26 51	0 0111	1 485	9 32	78 79	0 02097	0 17052	82 29	0 17786	85 89	0 18502
6	27 05	0 0111	1 457	9 53	78 90	0 02143	0 17045	82 41	0 17778	86 01	0 18494
8	28 18	0 0111	1 403	9 96	79 13	0 02235	0 17030	82 66	0 17763	86 26	0 18477
10	29 35	0 0112	1 351	10 39	79 36	0 02328	0 17015	82 90	0 17747	86 51	0 18460
12	30 56	0 0112	1 301	10 82	79 59	0 02419	0 17001	83 14	0 17733	86 76	0 18444
14	31 80	0 0112	1 253	11 26	79 82	0 02510	0 16987	83 38	0 17720	87 01	0 18429
16	33 08	0 0112	1 207	11 70	80 05	0 02601	0 16974	83 61	0 17706	87 26	0 18413
18	34 40	0 0113	1 163	12 12	80 27	0 02692	0 16961	83 85	0 17693	87 51	0 18397
20	35 75	0 0113	1 121	12 55	80 49	0 02783	0 16949	84 09	0 17679	87 76	0 18382
22	37 15	0 0113	1 081	13 00	80 72	0 02873	0 16938	84 32	0 17666	88 00	0 18369
24	38 58	0 0113	1 043	13 44	80 95	0 02963	0 16926	84 55	0 17652	88 24	0 18355
26	40 07	0 0114	1 007	13 88	81 17	0 03053	0 16913	84 79	0 17639	88 49	0 18342
28	41 59	0 0114	0 973	14 32	81 39	0 03143	0 16900	85 02	0 17625	88 73	0 18328
30	43 16	0 0115	0 939	14 76	81 61	0 03233	0 16887	85 25	0 17612	88 97	0 18315
32	44 77	0 0115	0 908	15 21	81 83	0 03323	0 16876	85 48	0 17600	89 21	0 18303
34	46 42	0 0115	0 877	15 65	82 05	0 03413	0 16865	85 71	0 17589	89 45	0 18291
36	48 13	0 0116	0 848	16 10	82 27	0 03502	0 16854	85 95	0 17577	89 68	0 18280
38	49 88	0 0116	0 819	16 55	82 49	0 03591	0 16843	86 18	0 17566	89 92	0 18268
39	50 78	0 0116	0 806	16 77	82 60	0 03635	0 16838	86 29	0 17560	90 04	0 18262
40	51 68	0 0116	0 792	17 00	82 71	0 03680	0 16833	86 41	0 17554	90 16	0 18256
41	52 70	0 0116	0 779	17 23	82 82	0 03725	0 16828	86 52	0 17549	90 28	0 18251
42	53 51	0 0116	0 767	17 46	82 93	0 03770	0 16823	86 64	0 17544	90 40	0 18245
44	55 40	0 0117	0 742	17 91	83 15	0 03859	0 16813	86 86	0 17534	90 65	0 18235
46	57 35	0 0117	0 718	18 36	83 36	0 03948	0 16803	87 09	0 17525	90 89	0 18224
48	59 35	0 0117	0 695	18 82	83 57	0 04037	0 16794	87 31	0 17515	91 14	0 18214
50	61 39	0 0118	0 673	19 27	83 78	0 04126	0 16785	87 54	0 17505	91 38	0 18203
52	63 49	0 0118	0 652	19 72	83 99	0 04215	0 16776	87 76	0 17496	91 61	0 18193
54	65 63	0 0118	0 632	20 18	84 20	0 04304	0 16767	87 98	0 17486	91 83	0 18184
56	67 84	0 0119	0 612	20 64	84 41	0 04392	0 16758	88 20	0 17477	92 06	0 18174
58	70 10	0 0119	0 593	21 11	84 62	0 04480	0 16749	88 42	0 17467	92 28	0 18165
60	72 41	0 0119	0 575	21 57	84 82	0 04568	0 16741	88 64	0 17458	92 51	0 18155
62	74 77	0 0120	0 557	22 03	85 02	0 04657	0 16733	88 86	0 17450	92 74	0 18147

TABLE XVI.—PROPERTIES OF DICHLORODIFLUOROMETHANE (F-12) \*—(Continued)

Sat temp., F	Abs press psia	Volume, ft <sup>3</sup> lb <sub>m</sub> <sup>-1</sup>		Specific enthalpy and entropy taken from -40 F							
				Specific enthalpy <i>h</i>		Entropy <i>s</i>		25 F superheat		50 F superheat	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	<i>h</i>	<i>s</i>	<i>h</i>	<i>s</i>
64	77 20	0 0120	0 540	22 49	85 22	0 04745	0 16725	89 07 0	17442	92 97 0	18139
66	79 67	0 0120	0 524	22 95	85 42	0 04833	0 16717	89 29 0	17433	93 20 0	18130
68	82 24	0 0121	0 508	23 42	85 62	0 04921	0 16709	89 50 0	17425	93 43 0	18122
70	84 82	0 0121	0 493	23 90	85 82	0 05009	0 16701	89 72 0	17417	93 66 0	18114
72	87 50	0 0121	0 479	24 37	86 02	0 05097	0 16693	89 93 0	17409	93 99 0	18106
74	90 20	0 0122	0 464	24 84	86 22	0 05185	0 16685	90 14 0	17402	94 12 0	18098
76	93 00	0 0122	0 451	25 32	86 42	0 05272	0 16677	90 36 0	17394	94 34 0	18091
78	95 85	0 0123	0 438	25 80	86 61	0 05359	0 16669	90 57 0	17387	94 57 0	18083
80	98 76	0 0123	0 425	26 28	86 80	0 05446	0 16662	90 78 0	17379	94 80 0	18075
82	101 70	0 0123	0 413	26 76	86 99	0 05534	0 16655	90 98 0	17372	95 01 0	18068
84	104 8	0 0124	0 401	27 24	87 18	0 05621	0 16648	91 18 0	17365	95 22 0	18061
86	107 9	0 0124	0 389	27 72	87 37	0 05708	0 16640	91 37 0	17358	95 44 0	18054
88	111 1	0 0124	0 378	28 21	87 56	0 05795	0 16632	91 57 0	17351	95 65 0	18047
90	114 3	0 0125	0 368	28 70	87 74	0 05882	0 16624	91 77 0	17344	95 86 0	18040
92	117 7	0 0125	0 357	29 19	87 92	0 05969	0 16616	91 97 0	17337	96 07 0	18033
94	121 0	0 0126	0 347	29 68	88 10	0 06056	0 16608	92 16 0	17330	96 28 0	18026
96	124 5	0 0126	0 338	30 18	88 28	0 06143	0 16600	92 36 0	17322	96 50 0	18018
98	128 0	0 0126	0 328	30 67	88 45	0 06230	0 16592	92 55 0	17315	96 71 0	18011
100	131 6	0 0127	0 319	31 16	88 62	0 06316	0 16584	92 75 0	17308	96 92 0	18004
102	135 3	0 0127	0 310	31 65	88 79	0 06403	0 16576	92 93 0	17301	97 12 0	17998
104	139 0	0 0128	0 302	32 15	88 95	0 06490	0 16568	93 11 0	17294	97 32 0	17993
106	142 8	0 0128	0 293	32 65	89 11	0 06577	0 16560	93 30 0	17288	97 53 0	17987
108	146 8	0 0129	0 285	33 15	89 27	0 06663	0 16551	93 48 0	17281	97 73 0	17982
110	150 7	0 0129	0 277	33 65	89 43	0 06749	0 16542	93 66 0	17274	97 93 0	17976
112	154 8	0 0130	0 269	34 15	89 58	0 06836	0 16533	93 82 0	17266	98 11 0	17969
114	158 9	0 0130	0 262	34 65	89 73	0 06922	0 16524	93 98 0	17258	98 29 0	17961
116	163 1	0 0131	0 254	35 15	89 87	0 07008	0 16515	94 15 0	17249	98 48 0	17954
118	167 4	0 0131	0 247	35 65	90 01	0 07094	0 16505	94 31 0	17241	98 66 0	17946
120	171 8	0 0132	0 240	36 16	90 15	0 07180	0 16495	94 47 0	17233	98 84 0	17939
122	176 2	0 0132	0 233	36 66	90 28	0 07266	0 16484	94 63 0	17224	99 01 0	17931
124	180 8	0 0133	0 227	37 16	90 40	0 07352	0 16473	94 78 0	17215	99 18 0	17922
126	185 4	0 0133	0 220	37 67	90 52	0 07437	0 16462	94 94 0	17206	99 35 0	17914
128	190 1	0 0134	0 214	38 18	90 64	0 07522	0 16450	95 09 0	17196	99 53 0	17906
130	194 9	0 0134	0 208	38 69	90 76	0 07607	0 16438	95 25 0	17186	99 70 0	17897
132	199 8	0 0135	0 202	39 19	90 86	0 07691	0 16425	95 41 0	17176	99 87 0	17889
134	204 8	0 0135	0 196	39 70	90 96	0 07775	0 16411	95 56 0	17166	100 04 0	17881
136	209 9	0 0136	0 191	40 21	91 06	0 07858	0 16396	95 72 0	17156	100 22 0	17873
138	215 0	0 0137	0 185	40 72	91 15	0 07941	0 16380	95 87 0	17145	100 39 0	17864
140	220 2	0 0138	0 180	41 24	91 24	0 08024	0 16363	96 03 0	17134	100 56 0	17856

\* IT Btu and lb<sub>m</sub> units, data are mainly from "Heating, Ventilating Air Conditioning Guide," American Society of Heating and Ventilating Engineers New York, 1947



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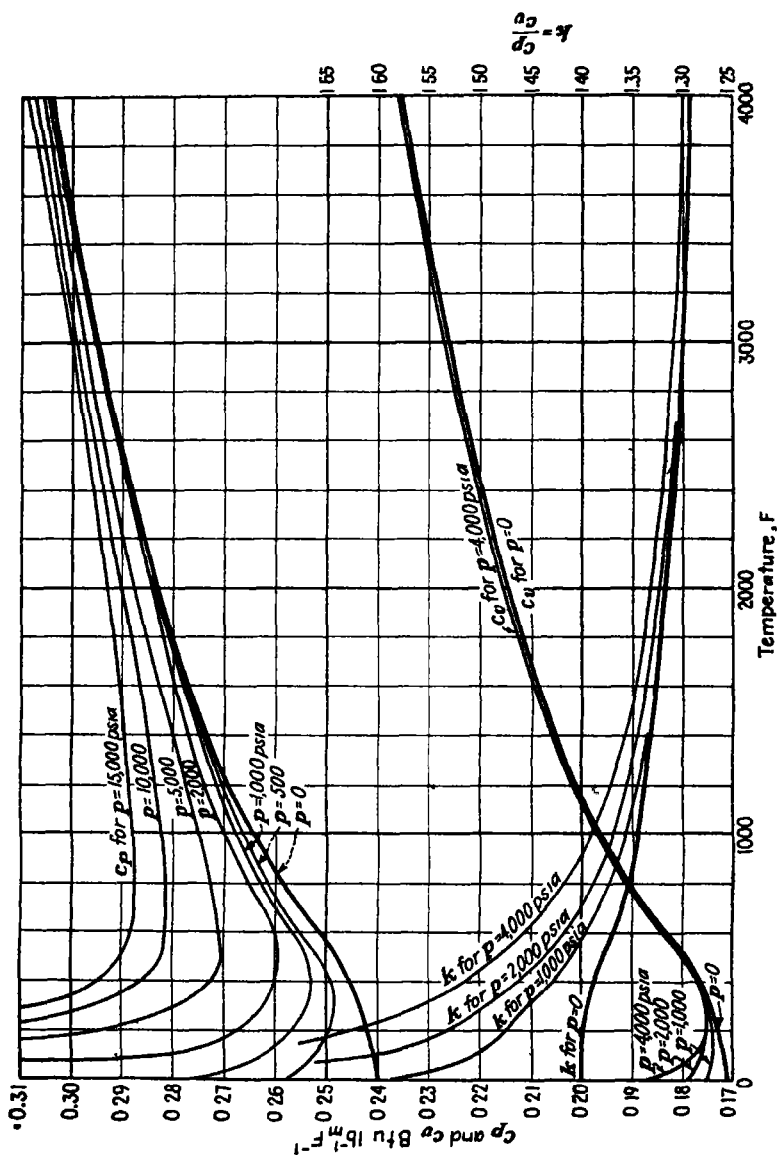
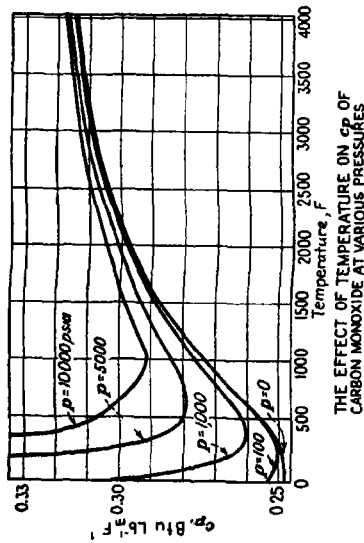


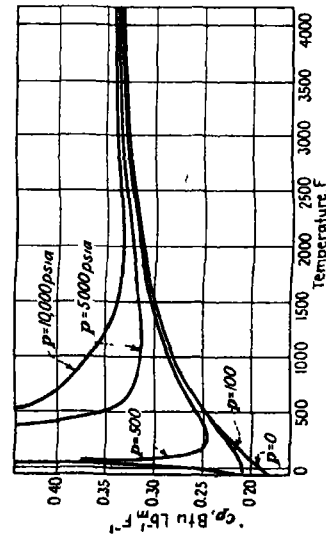
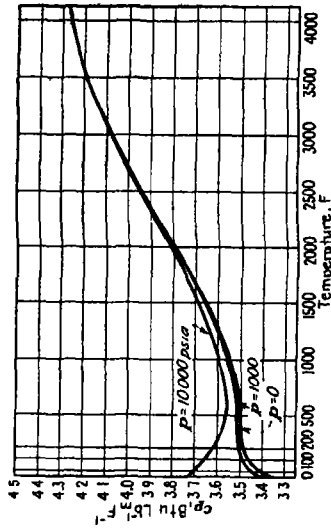
FIG 1A. The effect of temperature on  $c_p$  and  $c_v$  and  $k$  of dry air at various pressures (F. O. Ellenswood, N. Kulik, N. R. Gay, "The Specific Heats of Certain Gases over Wide Ranges of Pressures and Temperatures," Cornell Univ. Bulletin No. 30, Oct. 1942.)



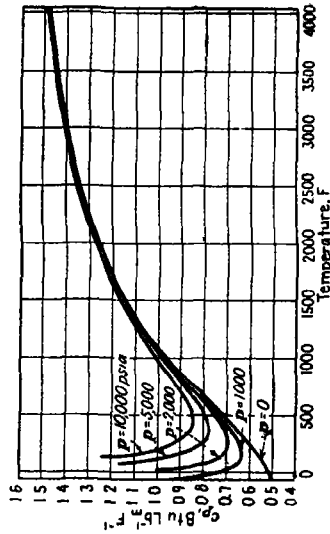




THE EFFECT OF TEMPERATURE ON  $c_p$  OF HYDROGEN AT VARIOUS PRESSURES



THE EFFECT OF TEMPERATURE ON  $c_p$  OF METHANE AT VARIOUS PRESSURES



THE EFFECT OF TEMPERATURE ON  $c_p$  OF

Fig 1B. The effect of temperature on  $c_p$  of various gases at various pressures (P. O. Ellenwood, N. Kulak, N. R. Gay, "The Specific Heats of Certain Gases over Wide Ranges of Pressures and Temperatures," Cornell Univ. Bulletin No. 30, Oct 1942)

$T R$  vs  $T R u$  /  $l b_m R$   
 AT CONSTANT PRESSURE  
 ATM. ABSOLUTE

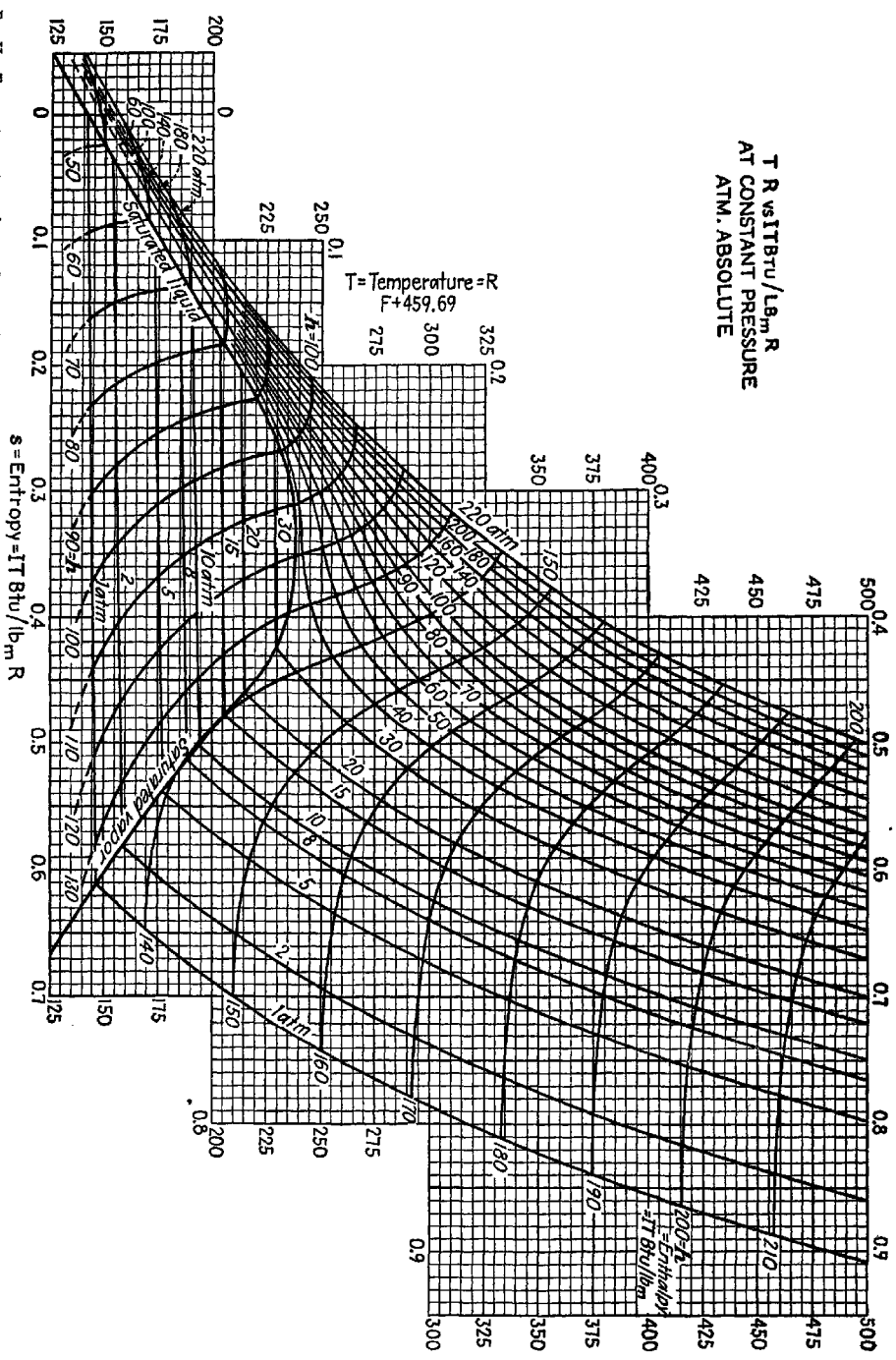


Fig. 11. Temperature-entropy diagram for air at low temperatures (T, C Williams, "The Thermodynamic Properties of Air at Low Temperatures," American Institute of Chemical Engineers, Vol. 38, No. 1, pp 88-111, Feb 1943)

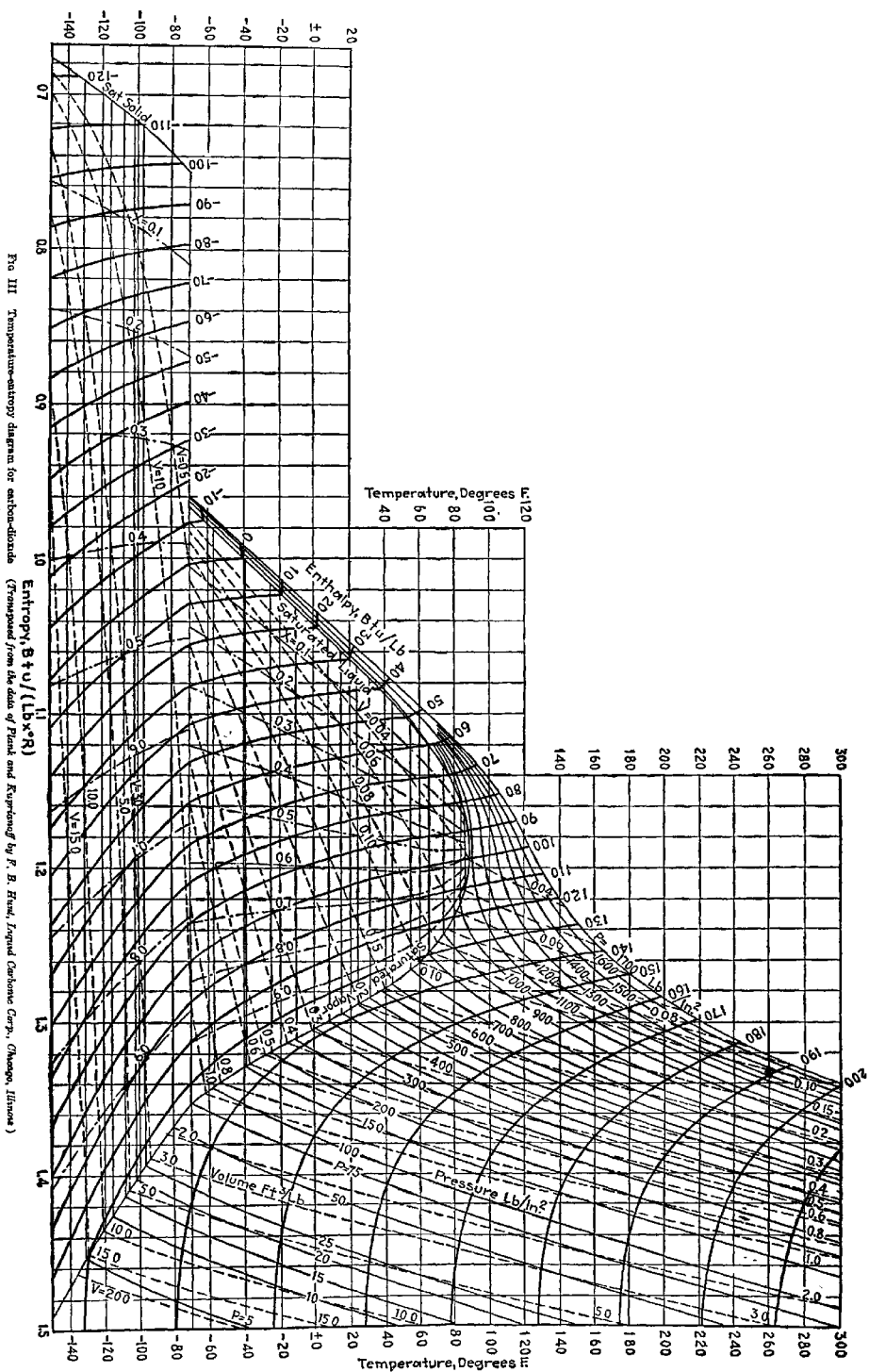


FIG. III Temperature-entropy diagram for carbon-dioxide (Temperatures from the data of Plank and Kyrsting by F. B. Hurl, Inland Carbonic Corp., Chicago, Illinois)

PRESSURE - psia

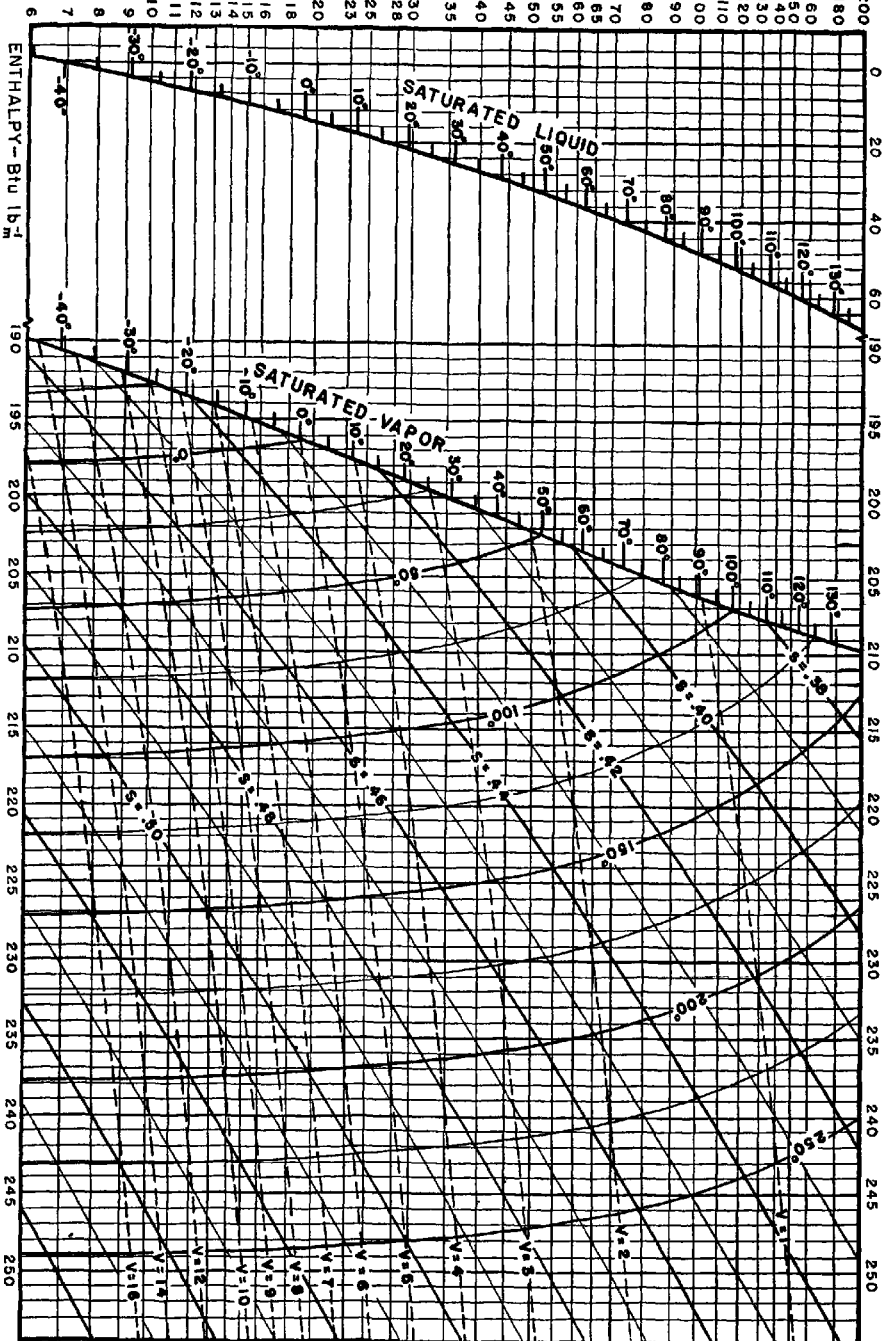
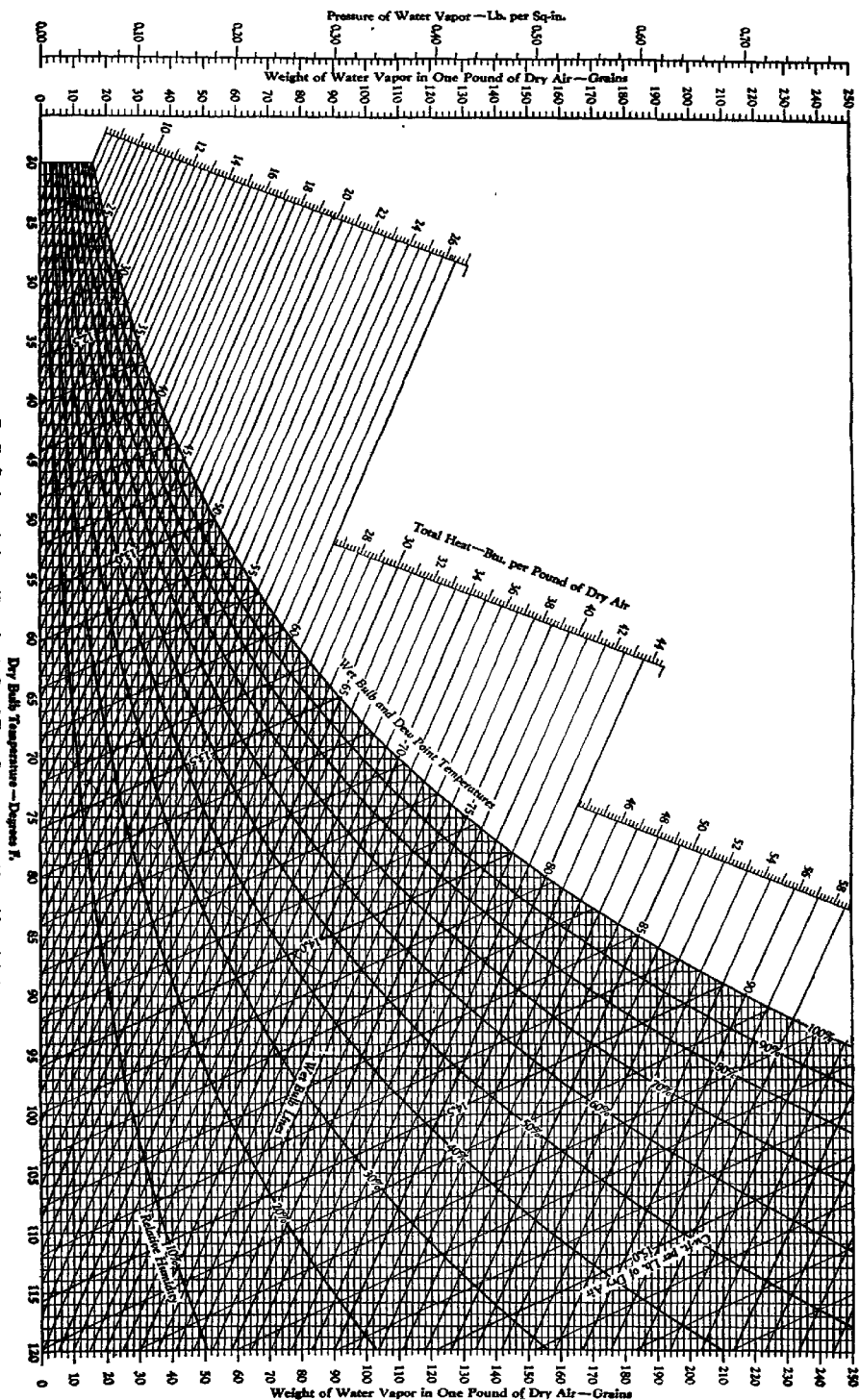


Fig. IV Pressure-enthalpy diagram for methyl chloride (By permission of R. I. DuPont de Nemours & Co., Inc., Wilmington, Delaware)



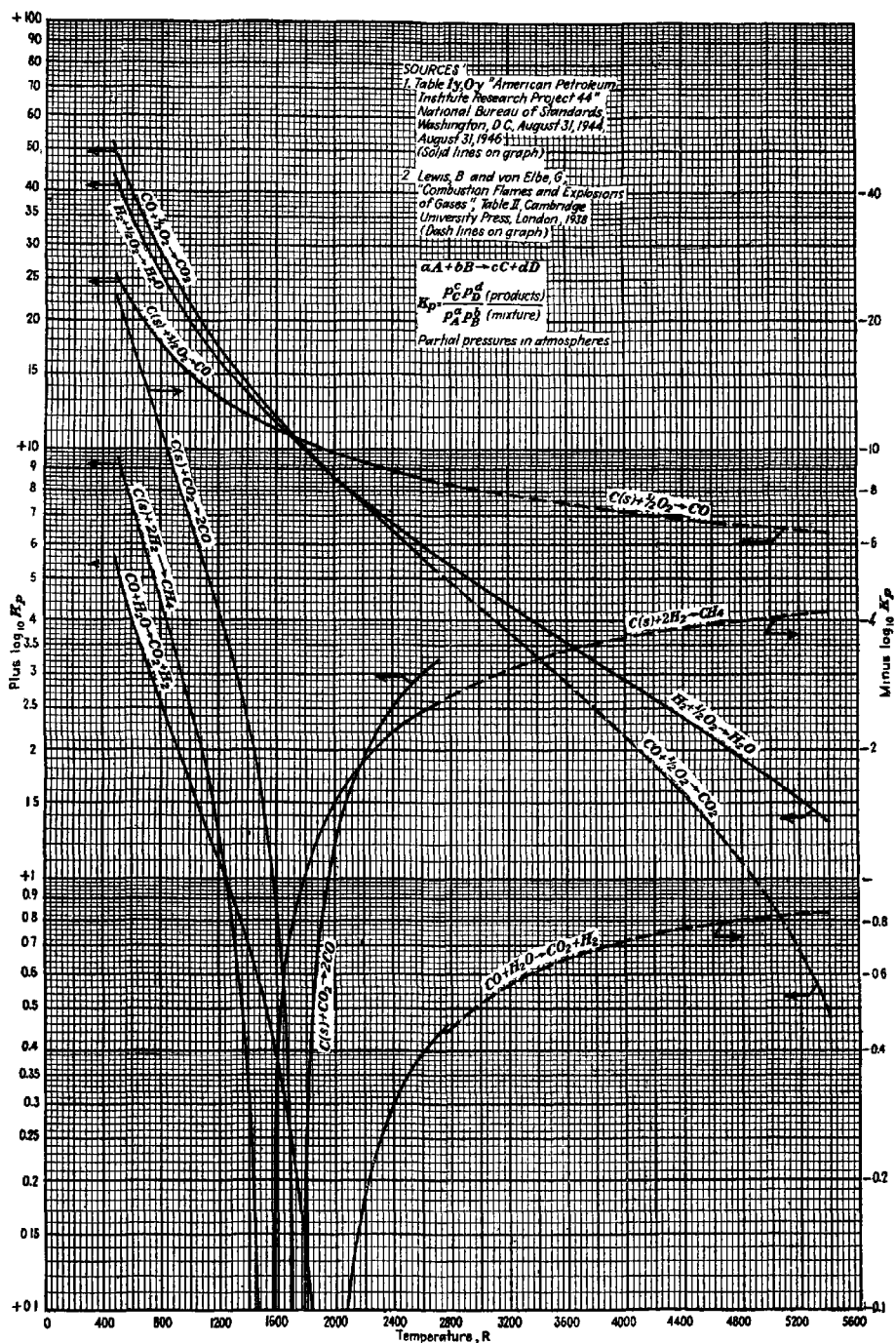


FIG. VI Equilibrium constants.

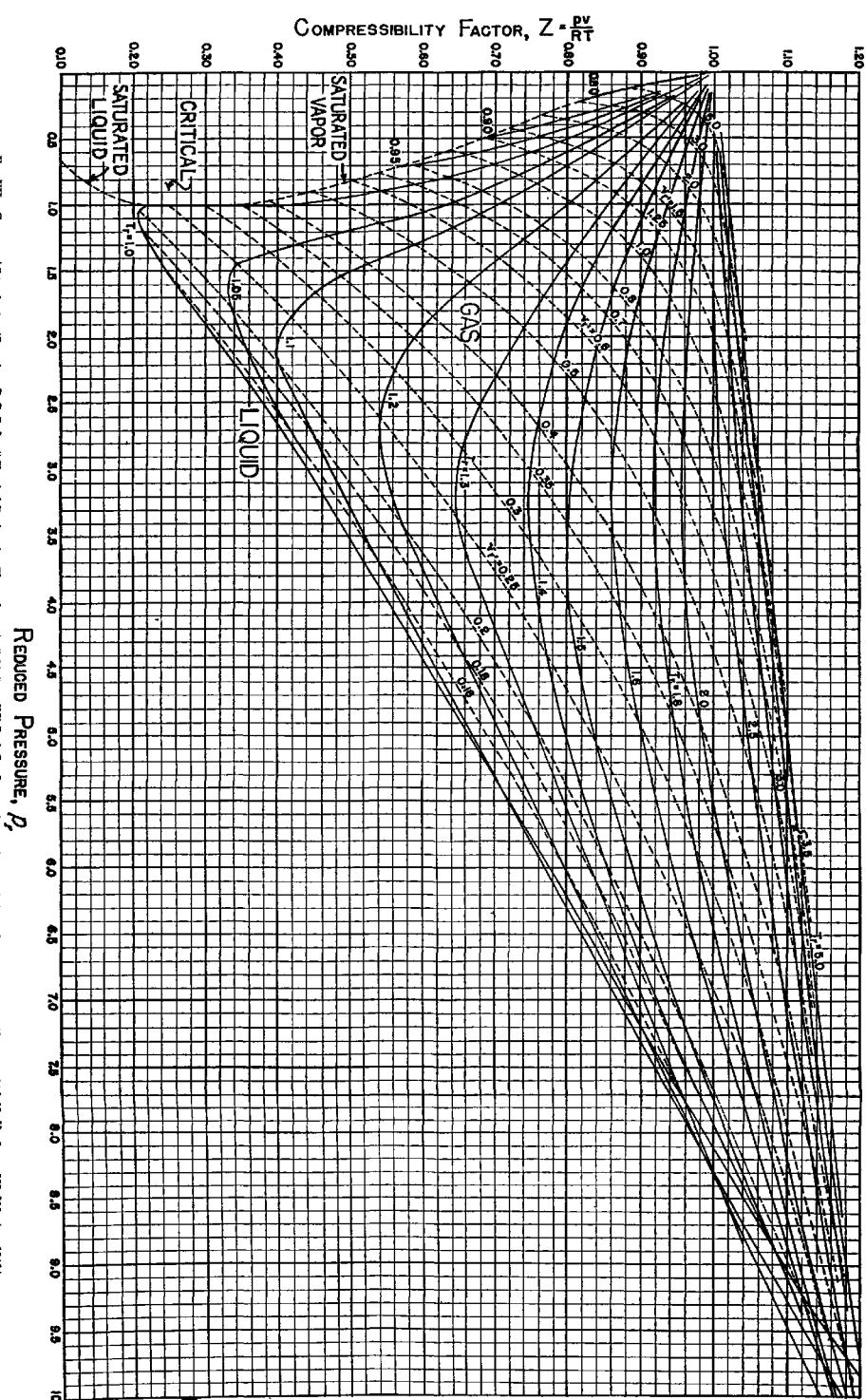


FIG. VII. Compressibility chart. (Data from B. P. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Co., Inc., and George N. S. Industrial and Engineering Chemistry, Vol. 38, No. 8, pp. 808-809, Aug. 1946.)



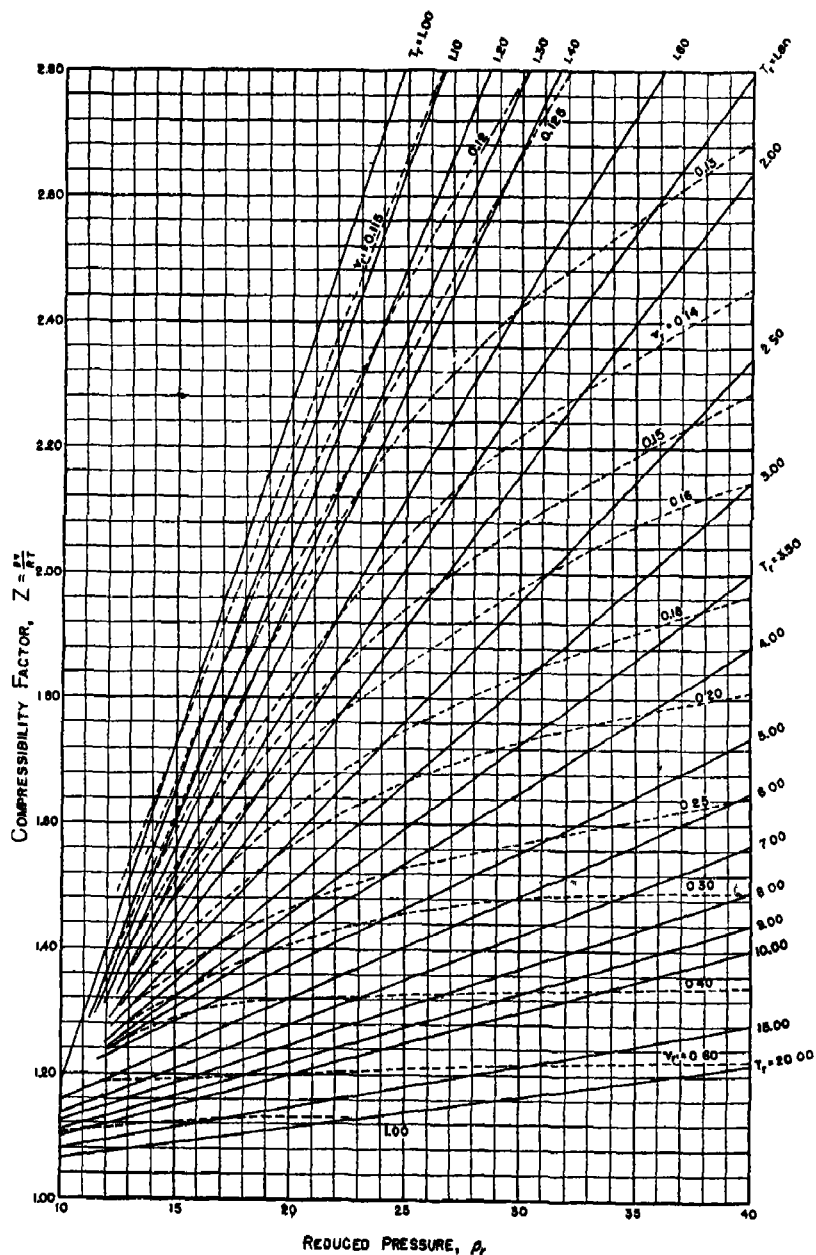


FIG VIII High pressure compressibility chart (Data from B F Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Co., Inc)

